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THE MEASUREMENT AND PREDICTION OF THE EFFECT OF PRESSURE ON ENTHALPY

by

© HENG-JOO NG

A THESIS

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TO MY FATHER

ABSTRACT

Accurate enthalpies of fluid mixtures over wide range of pressure and temperature are directly useful in design and provide an improved basis for the theories of fluids, improvement of methods of prediction, and for derivation of other thermodynamic properties. The purposes of this work are:

1) To construct a calorimeter for the existing recycle system to allow measurements on the isothermal effect of pressure on enthalpy.

2) To obtain accurate data on the effect of pressure on enthalpy for mixtures of methane with carbon dioxide, with carbon dioxide and nitrogen, with carbon dioxide and ethane, and with carbon dioxide, nitrogen and ethane.

3) To evaluate the available methods of prediction and to extend and improve the methods of prediction for the enthalpy of fluid mixtures.

An isothermal throttling calorimeter was chosen for measuring the effect of pressure on enthalpy. In common with several other throttling calorimeters, a capillary tube is used to cause the pressure drop. An insulated Nichrome wire which passes inside the capillary for its entire length serves to supply electrical energy. This arrangement makes the expansion essentially isothermal. The pressure drop across the calorimeter is measured by a differential pressure transducer and any temperature difference between the inlet and outlet is indicated by a calibrated thermopile.

Measurements were made with nitrogen as a test gas at four different temperatures from 273.15 to 374.15 K, and at pressures from 14 to 140 bar. The data are in good agreement with values from the literature. Measurements were made on the following six systems at pressures

from 14 to 140 bar: a) 14.5 mole percent of methane in carbon dioxide at temperatures of 0, 10, 20, 40, 60 and 90°C, b) 42.3 mole percent of methane in carbon dioxide at temperatures of 0, 40, 60 and 90°C, c) Equimolal mixture of methane, nitrogen and carbon dioxide at temperatures of -30, -10 and 10°C, d) Equimolal mixture of methane, carbon dioxide and ethane at temperatures of -10, 0, 20, 40, 60 and 90°C, e) methane rich mixture with carbon dioxide and ethane at temperatures of -10, 0, 20, 40, 60 and 90°C and, f) Equimolal mixture of methane, carbon dioxide, nitrogen, and ethane at temperatures of -30, -10, 10, 30 and 60°C.

Two enthalpy tables and diagrams for the two mixtures of methane and carbon dioxide were constructed which are based on this experimental work and that of Bishnoi.

The availability of more accurate enthalpy data based on calorimetric determinations provides an improved basis for comparison of available methods of prediction and the testing of the mixing rules. Nine enthalpy correlations were evaluated and compared. Three of the correlations used equations of state and six of the correlations used the corresponding states method of Curl and Pitzer with six different mixing rules. The six different mixing rules are: 1) Method of Barner and Quinlan, 2) Proposed Method, 3) Modified Method of Gunn, 4) Method of Prausnitz and Gunn, 5) Method of Joffe-Stewart, Burkhardt and Voo, and 6) Method of Leland and Mueller. The three equations of state are Starling-BWR, Soave-Redlich-Kwong and Mark V correlation. It was found that the equation of state of Starling-BWR, Soave-Redlich-Kwong, Mark V and the corresponding states correlation with pseudocritical parameters estimated by method 2, are the most accurate of the nine enthalpy correlations tested.

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INTRODUCTION

A knowledge of the enthalpies of fluid mixtures over a wide range of pressure and temperature is necessary for engineering designs and calculations of thermal processes. In the past, enthalpies used in process design were obtained principally from P-V-T data, either directly using thermodynamic relations or indirectly using equations of state. The process of generating enthalpies from compressibility data involves differentiation with attendant loss in accuracy of at least one order of magnitude. In a region where the derivatives are changing rapidly, such as the critical region, the error may be very large. In addition, accurate volumetric data for mixtures is still rather scarce, and the determination of enthalpy changes across the two-phase region involves the use of not only volumetric data and their derivatives, but also vapor-liquid equilibrium data and derivatives. For this reason it is desirable to have direct experimental determinations of the enthalpy behavior of fluid mixtures under pressure. These data are quite scarce in the literature.

The goal of this work was to construct a flow type calorimeter in a recycle system for the measurement of the isothermal effect of pressure on enthalpy. The isobaric effect of temperature on two binary mixtures of carbon dioxide and methane had been investigated by Bishnoi [9]. A specific purpose of the research has been to measure the isothermal effect of pressure on enthalpy of these two mixtures, so that it provides a thermodynamic consistency check and allows the construction of enthalpy tables for these two mixtures based on experimental data. In addition, experimental data of the isothermal effect of pressure on enthalpy were obtained for the following four systems: a) Equimolal carbon

dioxide-methane-nitrogen, (b) Equimolal carbon dioxide-methane-ethane, (c) methane-rich carbon dioxide-methane-ethane and (d) Equimolal carbon dioxide-methane-nitrogen-ethane.

There are many different methods of prediction which have been proposed for enthalpies of fluid mixtures. A comparative study has been made by Natural Gas Processors Association[79] on these numerous enthalpy correlations. The availability of more accurate enthalpy data based on calorimetric determinations provides an improved basis for comparison of available methods of prediction and the testing of the mixing rules.

To reiterate, the specific goals of the present research were (1) to construct a calorimeter for obtaining the isothermal effect of pressure on enthalpy, (2) to make experimental enthalpy determinations on two carbon dioxide-methane mixtures, one carbon dioxide-methane-nitrogen mixture, two carbon dioxide-methane-ethane mixtures and one carbon dioxide-methane-nitrogen-ethane mixture, (3) to evaluate the available methods of prediction and (4) to extend and improve the method of prediction for the enthalpy of fluid mixtures.

SECTION I - PRELIMINARY CONSIDERATIONS

In this section, a discussion of flow calorimetry and the necessary equations for ϕ which are applied, and a discussion of ϕ data in the literature are presented.

Flow Calorimeters

Measurements of the enthalpy of fluids at elevated pressures have been made by a number of methods. A review of experimental methods was presented by Barieau [4]. Flow calorimeters have many advantages and have been used widely. The calorimeter may be designed to operate in a number of differing modes depending upon the type of enthalpy data desired.

The first law of thermodynamics, applied to a flow calorimeter with negligible potential and kinetic energy effects, is

$$[\underline{H}_{T_2,P_2} - \underline{H}_{T_1,P_1}]_x = \frac{\dot{Q} - \dot{W}}{F} \qquad (1)$$

where $\dot{Q}$ is the rate of the heat transfer, $\dot{W}$ the rate of electrical energy transfer, and F is the mass flow rate. In the isobaric mode of operation, the pressure difference P_2-P_1 is made small and the fluid is heated to change its temperature. Equation (1) becomes:

$$[\underline{H}_{T_2} - \underline{H}_{T_1}]_{P_1,x} = -\frac{\dot{W}}{F} - \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial P}\right)_T dP \Big|_{T_1} \qquad (2)$$

where the integral term is a small correction for the fact that the pressure is not constant, and $\dot{Q}$ is assumed to be negligible.

In the isenthalpic mode, no energy is added to the system and the heat leak is made negligible. For this case Equation (1) reduces to

$$[\underline{H}_{T_2,P_2} - \underline{H}_{T_1,P_1}]_x = 0 \qquad (3)$$

In the isothermal mode of operation, a pressure drop is imposed on the fluid, and energy is added so that the outlet temperature is equal to the inlet temperature. It is practical to utilize this scheme only when the Joule-Thomson coefficient is positive, i.e. when the fluid cools upon expansion. For an isothermal operation, Equation (1) becomes:

$$[\underline{H}_{P_2} - \underline{H}_{P_1}]_{T_1} x = \frac{\dot{W}}{F} - \int_{T_1}^{T_2} C_P \, dT\Big|_{P_2} \tag{4}$$

where $\dot{Q}$ is assumed negligible and the integral corrects for any mismatch between the inlet and outlet temperatures. In this operation, a knowledge of the flow rate, the energy input and pressure drop are needed to determine the isothermal effect of pressure on enthalpy.

The enthalpy change on mixing can be determined in a flow calorimeter by mixing two pure gases in a chamber and adding electrical energy to equalize the inlet and outlet temperatures. The first law of thermodynamics for this calorimeter reduces to:

$$[\underline{H}_{mix}]_{T_2,P_2} - [x_1\underline{H}_1 + x_2\underline{H}_2]_{T_1,P_1} = \frac{\dot{Q} - \dot{W}}{F} \tag{5}$$

Corrections can be made for the differences in pressure and temperature between the inlet and outlet. The excess enthalpy or heat of mixing can be determined by:

$$\underline{H}^E = [\underline{H}_{mix} - x_1\underline{H}_1 - x_2\underline{H}_2]_{P,T} \tag{6}$$

Thermodynamic Relations

The relations presented above involve integral changes in enthalpy. These integral data in a single phase region may be interpreted to yield the derivative properties. Point values of the isothermal

throttling coefficient ϕ are estimated from the integral values by application of the following relation from Equation (4),

$$\phi \equiv \left(\frac{\partial H}{\partial P}\right)_{T,x} = \lim_{P_2 \to P_1} \left[\frac{H_{P_2} - H_{P_1}}{P_2 - P_1}\right]_{T,x} \tag{7}$$

The isothermal throttling coefficient can be estimated from known values of other thermodynamic properties. Thus, in making use of P-$\underline{V}$-T data the following identity applies:

$$\phi = \underline{V} - T\left(\frac{\partial \underline{V}}{\partial T}\right)_P \tag{8}$$

The identity involving μ, the Joule-Thomson coefficient and C_P, the isobaric heat capacity, provides another method of calculating ϕ. The functional relations between the enthalpy, the pressure and the temperature are:

$$\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_H \left(\frac{\partial T}{\partial H}\right)_P = -1$$

or

$$\left(\frac{\partial H}{\partial P}\right)_T = -\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P$$

or

$$\phi = -\mu C_P \tag{9}$$

The virial equation of state is a power series in density:

$$\frac{P\underline{V}}{RT} = 1 + \frac{B}{\underline{V}} + \frac{C}{\underline{V}^2} + \ldots \tag{10}$$

The terms B, C, ... are known as the second, third, ... virial coefficients and they are related by the statistical theory of imperfect gases to the interactions of molecules in pairs, triplets, etc.

A similar power series is an expansion in pressure:

$$\frac{PV}{RT} = 1 + B'P + C'P^2 + \ldots \tag{11}$$

The coefficients of the two series are related by

$$B' = \frac{B}{RT}$$

$$C' = \frac{(C - B^2)}{(RT)^2} \tag{12}$$

Using Equation (8), (10), (11) and (12), ϕ can be expressed as:

$$\phi = -RT^2 \left[\frac{dB'}{dT} + P \frac{dC'}{dT} + \ldots\right]$$

or

$$\phi = (B - T\frac{dB}{dT})(1 - \frac{2B}{RT} P + \frac{6B^2}{(RT)^2} P^2) + \frac{1}{RT} (2C - T \frac{dC}{dT})P + \ldots \tag{13}$$

The zero-pressure value of the isothermal throttling coefficient is finite and depends only on B:

$$\phi^\circ = B - T(\frac{dB}{dT}) \tag{14}$$

Experimental values of ϕ° can be used to derive changes in B upon integration of Equation (14):

$$B_{T_2} = T_2 \left[\int_{\tau_1}^{\tau_2} \phi^\circ(\tau) d\tau + B_{T_1} \tau_1\right] \tag{15}$$

where $\tau = 1/T$. Experimental values of ϕ° can be compared with values of ϕ° calculated from virial coefficients obtained from other type of experiments. For mixtures, B is of the form:

$$B_{mix} = \sum_i \sum_j x_i x_j B_{ij} \tag{16}$$

where B_{ii} and B_{jj} are the pure component second virial coefficients and B_{ij} is the interaction second virial coefficient. It follows that the derivative of B_{mix} is:

$$\frac{dB_{mix}}{dT} = \sum_i \sum_j x_i x_j \left(\frac{dB_{ij}}{dT}\right) \qquad (17)$$

Previous Experimental Data for ϕ

All of the above methods have been used to obtain thermal data of fluids at elevated pressures. Most of the results have been for pure components. A recent review of available pure components and mixtures data at elevated pressures have been presented by Mather [57] and Yesavage [97]. Table I presents a listing of the experimental determinations of thermal properties under pressure by isothermal calorimeter, supplementing that of Mather [57]. Although an increased amount of enthalpy data are available, the need for more data to test methods of prediction and improve correlations remains.

TABLE I

Recent References to Isothermal Effect of Pressure on Enthalpy of Fluid Under Pressure

Year	System	Author	References
1967	Nitrogen		
	Propane-methane	Mather et al.	57, 58, 59
1968	Propane		
	Propane-methane	Yesavage et al.	97, 98, 99, 100
1968	Methane-propane	Dillard et al.	22
1969,70	Carbon dioxide	Vukalovich et al.	86, 87, 88
1970	Methane-ethane	Alkasab	2
1970	Methane-ethane-propane	Furtado et al.	26
1972	Carbon dioxide-nitrogen	Vukalovich et al.	89
1973	Ethane	Miyazaki	61a
1974	Methane-carbon dioxide		
	Methane-carbon dioxide-ethane		
	Carbon dioxide	Peterson & Wilson	68

SECTION II - THE CALORIMETER AND THE FLOW SYSTEM

A review of the previous work employing isothermal throttling calorimeters is presented here. The design of a new throttling calorimeter and the experimental equipment are discussed in this section.

Background on Isothermal Throttling Calorimetry

All methods for measuring the isothermal effect of pressure on enthalpy involve some device to cause the pressure drop and a source of energy to compensate for the cooling effect resulting from the pressure drop. So, the methods are suitable only when ϕ is negative and no isothermal calorimeters have been designed to extract energy if the fluid warms on expansion.

A review of the development in isothermal throttling calorimetry had been presented by Mather [57]. In general, a porous media, a needle valve or a capillary tube is used to cause the pressure drop, and the electric heating coil is used as a source of energy.

The calorimeter designed by Mather [57] consists of a capillary coil to cause the pressure drop and the insulated heating wire is placed inside the capillary. Measurements were made on nitrogen and a mixture of propane and methane in the temperature range from -140°F to 200°F and in the pressure range from 100 to 2000 psia. Yesavage [97] used the same equipment to make measurements on propane and propane-methane mixtures.

Vukalovich et al. [86,87] reported the measurements on carbon dioxide by using adjustable needle valve with pressure drop up to 50 atm. Later on, Vukalovich et al. [88] designed a different type of calorimeter in which the throttling unit is pressure-relieved. Again the adjustable needle valve was used as the throttling unit.

Alkasab [1] designed an adjustable needle valve to study the isothermal throttling effect of methane-ethane mixtures.

Peterson and Wilson[68] constructed an integral isothermal throttling calorimeter by using throttling valve to cause the pressure drop. Measurements were made on pure carbon dioxide, and mixtures of equimolal methane-carbon dioxide, equimolal methane-ethane-carbon dioxide.

Eakin and DeVaney [25] designed a calorimeter which permits measurement of the Joule-Thomson coefficient, the isothermal enthalpy change on throttling and the isobaric enthalpy change. The idea of tubing packed with powder was used to cause the pressure drop. This idea was first used for Joule-Thomson experiments by Dawe and Snowdon[21].

Design of Isothermal Throttling Calorimeter

The first requirement in the design of the calorimeter was that it should operate over a wide range of temperatures from -100°C to 200°C and at any pressure in this temperature range from 100 to 2000 psia. Stainless steel was selected as the material of construction because of anticipated subsequent experimental work with corrosive gases and its strength at low temperature.

Since the design was to allow for the possibility of measuring isothermal enthalpy changes across a two-phase region, the use of throttling valve was abandoned because the instability of two-phase flow through a valve caused by alternate slugs of liquid and vapor prevents accurate thermodynamic measurements.

A capillary was considered to be the best configuration for the throttle because the expansion is smooth and if energy is added to the fluid during expansion, the process will be almost isothermal. Since

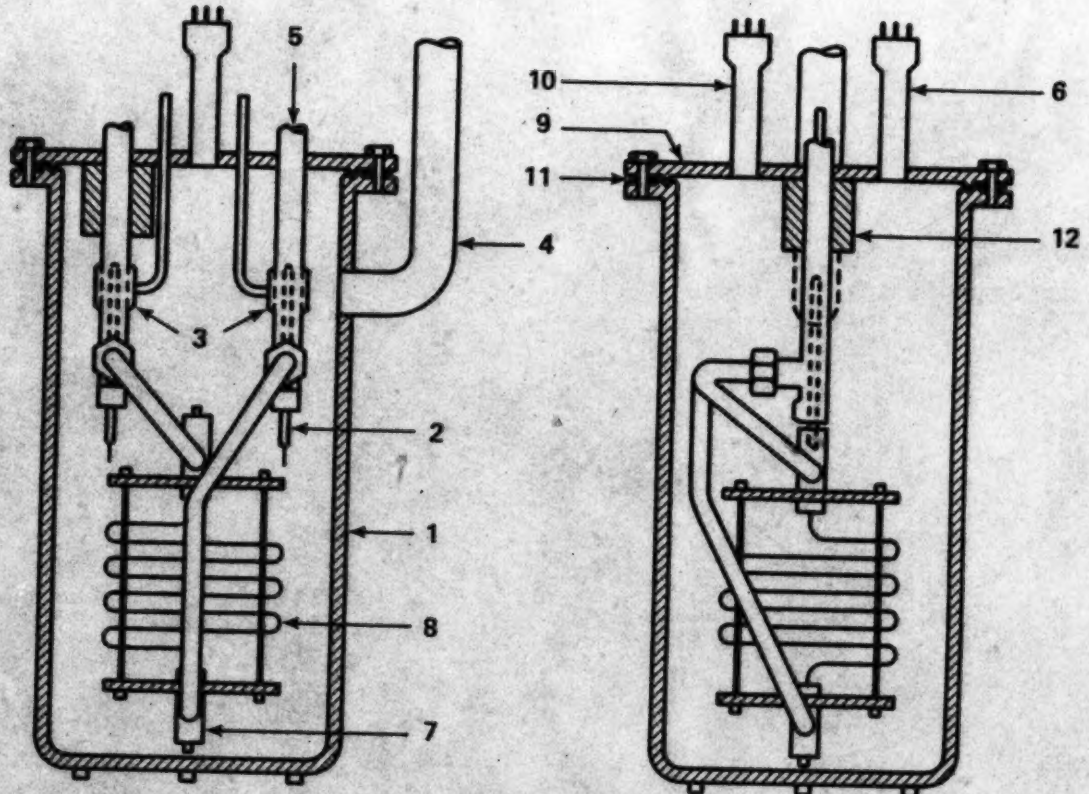
enthalpy is a point function, it is not necessary for the expansion to be isothermal. However, by making the path as nearly isothermal as possible, heat leakage from the surroundings to the system is minimized.

The disadvantage of capillary throttle is that it is not possible to vary flow rate and pressure drop independently. The disadvantage can be overcome by making the capillary removable so that various combinations of pressure drop and flow rate may be obtained.

The heater of the present calorimeter is an insulated Nichrome wire which passes inside the capillary for its entire length. Two copper power leads are connected to the heater wire at the ends of the capillary. In order to minimize the power losses through the leads the current must be kept low. The combination of heater size and capillary size allows different pressure drop and power input relations. With this arrangement, currents were kept below two amperes.

Description of the Calorimeter

The isothermal throttling calorimeter of this work is shown in Figure 1. The fluid enters the vacuum jacket from the constant temperature bath. The pressure tap at the inlet portion of the calorimeter serves to measure the inlet pressure and a differential thermocouple is used to check the temperature between the inlet portion of the calorimeter and the bath. Then the fluid passes through the throttling portion. A removable capillary coil at the throttling portion causes the pressure drop. The outlet temperature of the fluid is brought back to the inlet temperature by applying power to the Nichrome wire, which is placed inside the capillary. In this work, three different capillary sizes are employed of 15 BWG, 16 BWG and 17 BWG hypodermic tubing, all about ten feet in



1. vacuum jacket
2. thermopiles
3. pressure tap
4. vacuum line
5. gas line
6. heater leads
7. Conax gland
8. capillary coil
9. cover
10. thermopile leads
11. Teflon gasket
12. aluminum block

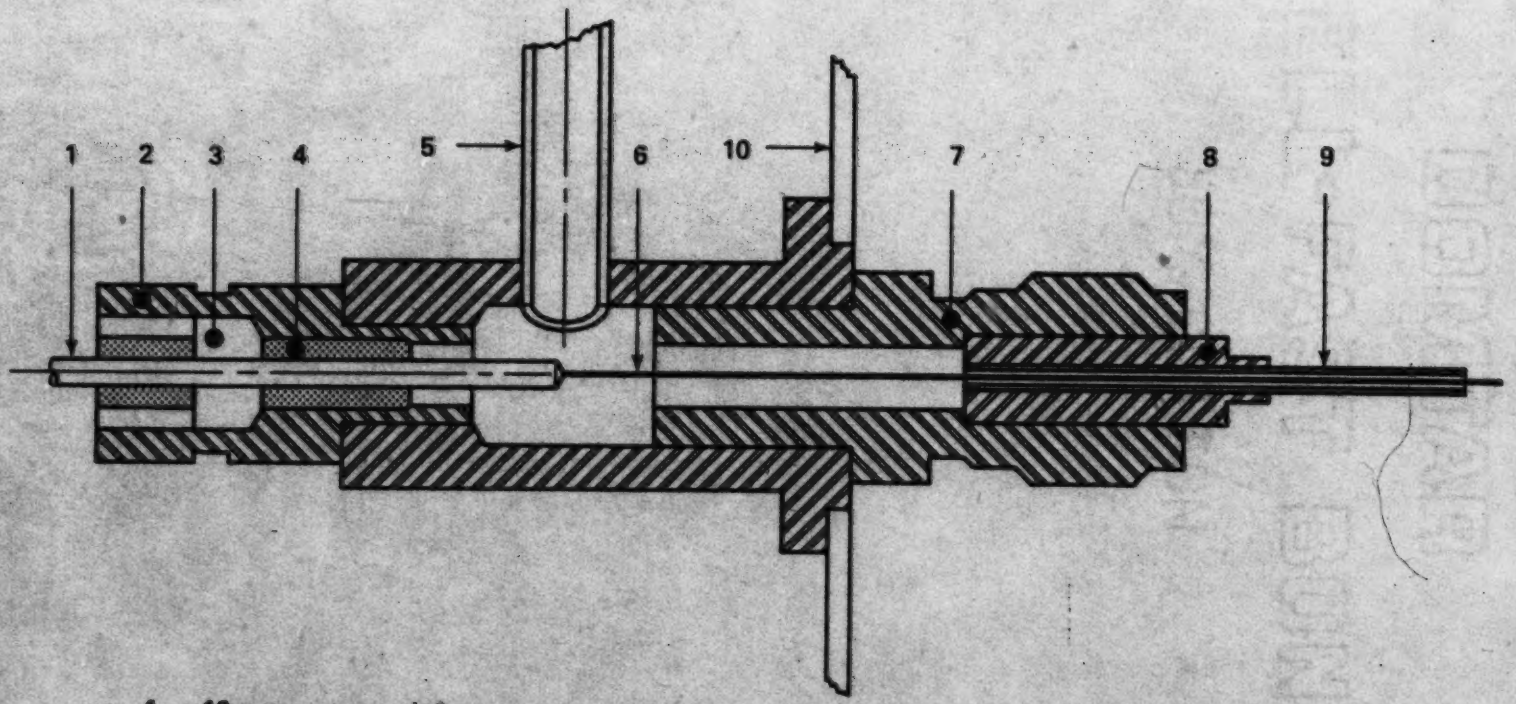
FIGURE 1. Assembly Drawing for Isothermal Throttling Calorimeter

length. Two different sizes of Nichrome wire, 36 and 40 gauge, are used. A five junction differential thermopile is used to determine the equality of inlet and outlet temperature. The pressure drop is determined by the differential pressure transducer. As shown in Figure 1, all the pressure and temperature measurements are at the same elevation. The lead wires of the heater and the thermopile are wrapped around a massive aluminum thermal equalization block. The heater wire leads are brought from the vacuum jacket into both ends of the capillary by Conax connectors. The detail drawing of this portion is shown in Figure 2.

Other efforts were made to reduce heat transfer to the surroundings. A radiation shield completely enclosed the capillary coil. The power leads and thermopile leads are brought into contact with the vacuum jacket. The entire jacket is evacuated to less than five microns through the vacuum line.

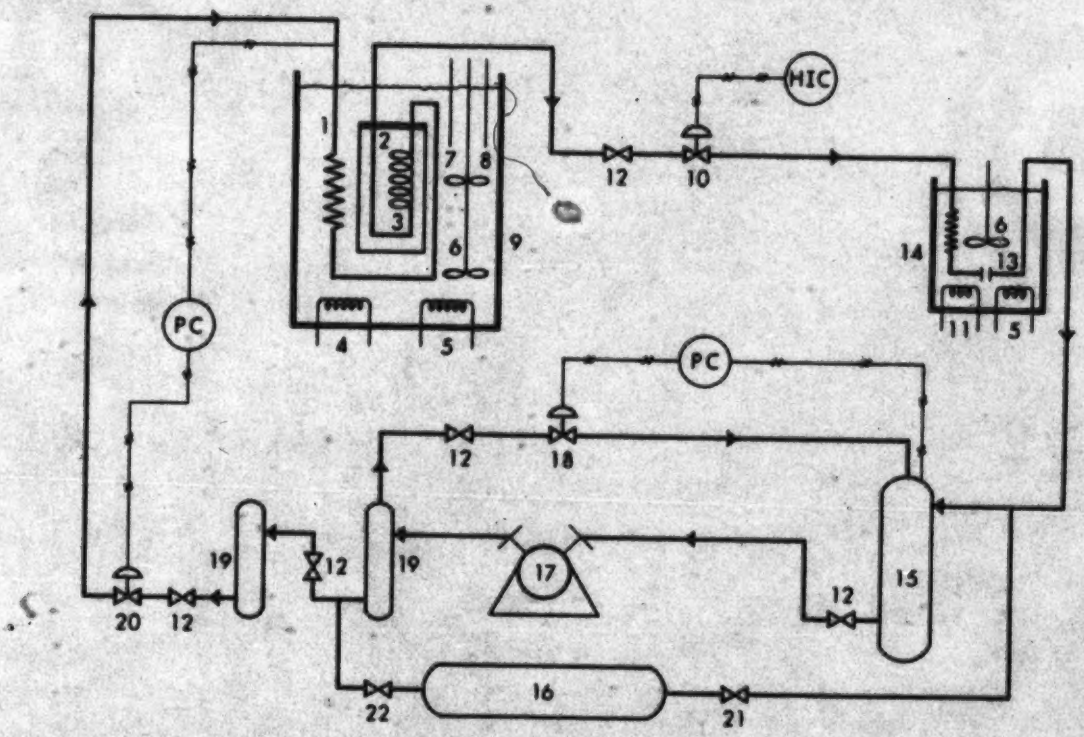
Experimental Equipment

The calorimeter is part of a recycle system, the evolution of which can be traced in the thesis of Bishnoi [9]. The recycle system serves to bring the fluid under investigation to the desired conditions of pressure and temperature for measurements. A schematic diagram of the flow system is shown in Figure 3. The fluid delivered by the compressor goes to the high pressure storage tanks, one of which is connected to the low pressure surge tank through the by-pass control valve BPCV. The fluid leaving the surge tanks goes to a hand valve and the high pressure control valve HPCV. The fluid passes through a long cooling coil before it enters the calorimeter. The cooling coil and the calorimeter are in the same bath. The pressure at the inlet of the calorimeter is governed



1. 16 gauge copper wire
2. Conax connector
3. Teflon sealant
4. ceramic insulators
5. ¼" O.D. S.S. tube
6. glass fabric insulated Nichrome wire
7. ¼" Swagelok connector
8. S.S. adapter
9. 17 gauge S.S. capillary tube
10. end plate

FIGURE 2. Detail Drawing for the Ends of the Capillary of the Calorimeter



LEGEND

1. Inlet tubing for the Calorimeter
2. Isothermal Calorimeter
3. Capillary Tubing
4. Liquid Nitrogen Cooling
5. Controlled Heat Input
6. Stirrer
7. Platinum Thermometer
8. Sensor for Heat Input Controller
9. Temperature Bath for the Calorimeter
10. Joule Thomson Control Valve
11. Water Cooling
12. Hand Valve
13. Orifice Meter
14. Temperature Bath for the Flow Meter
15. Low Pressure Tank
16. Storage Tank
17. Corblin Diaphragm Compressor
18. By-pass Control Valve
19. High Pressure Tank
20. High Pressure Control Valve
21. Feed Valve
22. Discharge Valve

FIGURE 3. Flow Diagram of the Apparatus

by the set point of the high pressure controller. The outlet stream of the calorimeter goes through a hand valve and the control valve JTCV. The opening of JTCV, manipulated manually, gives the desired mass flow rate of the fluid through the calorimeter. The fluid is then passed through the flow meter. The constant inlet pressure of the flow meter is controlled by the BPCV valve which is governed by the set point of the controller. Then the fluid passes through a low pressure storage tank before returning to the intake of the compressor.

Auxiliary Equipment

1. Control Valves and Pressure Control

It was necessary to control the pressure of fluid entering the calorimeter and the flow meter. For flexibility, the low pressure control scheme should be such that it could maintain the pressure anywhere in the range of 10 to 50 psig. The high pressure control scheme was required to maintain any pressure up to about 3000 psig. Both the schemes should also be able to handle flow rates ranging from one to four standard cubic feet per minute for different gases such as methane, nitrogen, carbon dioxide, ethane or their mixtures.

Figure 3 gives the location of HPCV, the high pressure control valve, JTCV, the pressure reducing control valve and BPCV, the by-pass control valve. These valves were sized by the standard method of C_v (valve flow coefficient) calculations. The valves used are:

HPCV - Annin valve model 9460, trim size 0.02, air-to-close, can handle fluids from -400 to 750°F.

JTCV - Annin valve model 9460, trim size 0.003, air-to-open, can handle fluids from -400 to 750°F.

BPCV - Annin valve model 5061 "Wee-Willie", trim size "A" - C_v range 0.0001 to 0.01, field reversible, can handle fluids from -200 to 465°F.

The valves had pneumatic positioners and stainless steel type 316 bodies.

For both HPCV and BPCV, single feed back control loops having a controller with a proportional constant and an integral constant were used. Foxboro controllers with built-in power supplies were used for the high and low pressure controls. High and low pressures were measured, at the locations shown in Figure 3 , by Foxboro pressure transmitters model 611 GH and 611 GM respectively. The current to pressure converters used in the pressure control loop are Fisher type 546 electro-pneumatic transducers.

The resistance of the valve JTCV was adjusted to give the desired flow rate by manually setting a potentiometer which supplied a current signal to the current-to-pressure converter, giving an air pressure to the valve positioner. Since the upstream pressure of JTCV and its resistance remained constant and the flow through the valve was sonic, this scheme gives constant mass flow rate through the calorimeter.

2. *Material Recirculating Device*

A two-stage diaphragm compressor was used to develop the necessary pressure and to circulate the fluids. It was a Corblin A2CV250 which was rated for a discharge pressure of up to 3700 psig with a flow capacity of 3.5 scfm at a suction pressure of 14.7 psia. The inlet and delivery lines of the compressor were connected to the tanks by means of flexible pipes.

3. *Gas Heaters*

In order to maintain the steady-state operation, the control valves HPCV, BPCV and JTCV were maintained at constant opening. The pressure drop across the "HPCV" valve ranged from 50 to 400 psi and a strip heater was used to compensate the cooling effect due to the pressure drop. Since cooling effect is large because of pressure drop across the BPCV and JTCV ranged from 300 to 2000 psi, steam heaters were used to heat the fluid before it passed through the valves.

4. *Temperature Controller*

The calorimeter bath temperatures were controlled within ±0.01°C by a Hallikainen Thermotrol temperature controller, model 1053.

Measuring Instruments

1. The temperature of the bath was determined by using a Leeds and Northrup platinum resistance thermometer, model number 8163 and it was calibrated for use in the range 90.188 K < T < 773.15 K on the International practical temperature scale of 1968 by National Research Council of Canada.

2. The inlet temperature of the fluid to the calorimeter was assumed to be equal to the bath temperature and a one-junction copper-constantan differential thermocouple was used to check the measurement. The temperature difference between inlet and outlet was measured by a five-junction copper-constantan differential thermopile. Both the one-junction thermocouple and the five-junction thermopile were calibrated for the zero reading at boiling and ice temperatures of water, and the melting temperature of dry ice. A d-c null voltmeter was used to read

the null point for the thermopile. The accuracy of the temperature measurement is about ±0.01°C.

3. The inlet pressure was measured by a Heise gauge and the pressure drop across the calorimeter was determined by a Validyne differential pressure transducer. Both Heise gauge and pressure transducer were calibrated by the Ruska dead weight tester. The accuracy of the gauge is 0.1 percent of full scale, and the accuracy of the pressure transducer is 0.5 percent of the full scale.

4. The electrical energy input to the calorimeter was supplied by Kepco DC power supply and was measured by a Hewlett-Packard model 3450 multifunction meter with the six-digit display.

5. In the early stage of this work a Nupro "F" inline filter was used as a flow meter. The mass flow rate for nitrogen and 42.3% methane in carbon dioxide mixture was determined from the inlet pressure and the pressure drop across the filter together with the constant temperature at the element. These data were used to solve the calibration equation:

$$\frac{P_1^2 - P_2^2}{Z\mu' F} = A + B\left[\frac{FM}{\mu'}\right] \tag{18}$$

for the mass flow rate F. The constants A and B were obtained from a least square fit of the calibration data obtained by the gasometer, where P_1 and P_2 are the inlet and outlet pressure of the flow meter which are given by pressure transducers. μ', Z and M are the viscosity, compressibility and molecular weight of the gas respectively.

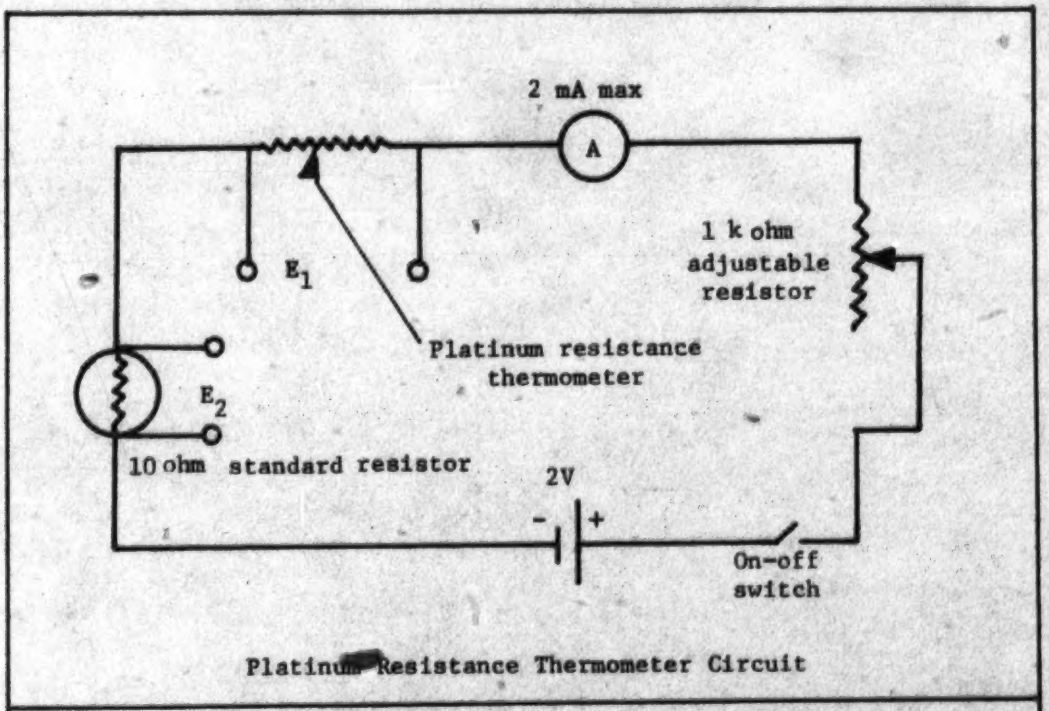
During the data taking of the 42.3% methane in carbon dioxide mixture, it was found that the solid contamination in the flow meter element causes the changing of the calibration curve. The flow meter was recalibrated and after obtaining the experimental data of the mixture,

the flow meter was recalibrated again. It was found that the two calibration curves disagreed by 0.8 percent. So, the filter was abandoned as device for the flow measurement. The average mass flow rate calculated by the two calibration curves was used to reduce the experimental data of this mixture.

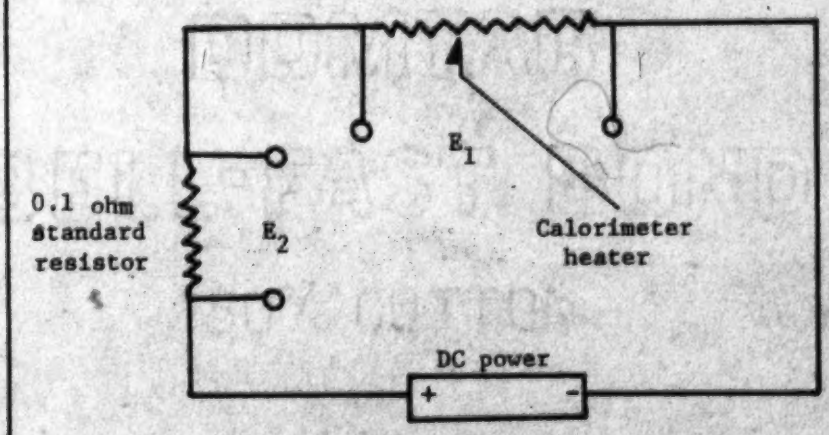
A square-edged orifice was then used for the flow measurement. The orifice had a diameter of 0.16 in. and it was located in a 1/2 in. tube with an inside diameter of 0.429 in. The inlet pressure was maintained constant by the BPCV control valve, and was determined by a Validyne pressure transducer. The pressure drop across the orifice was measured by a Foxboro d/p cell transmitter type 613 M. The accuracy of the pressure transducer and d/p cell is 0.5 percent of the full scale. The orifice was calibrated using pure nitrogen, methane, ethane and carbon dioxide and argon by the gasometer. The orifice was calibrated at the completion of the experiments on every mixture using the gas mixture itself. The overall standard deviation of the flow rate is about 0.5 percent. The calibration of the orifice is given in Appendix A.

All the output signals of the presure transducers, d/p cell transmitter, platinum resistance thermometer, power to the calorimeter and thermopile were connected to a Hewlett-Packard model 3450 multi-function meter by a multi-junction selection switch.

Figure 4 shows the electric circuits of platinum resistance thermometer and the calorimeter heater.



Platinum Resistance Thermometer Circuit



Calorimeter Heater Circuit

Figure 4: Wiring Diagram of Platinum Resistance Thermometer and Calorimeter Heater Circuits

SECTION III - EXPERIMENTAL RESULTS AND DISCUSSION

In this section, the experimental procedure, the materials used, and a summary of the techniques used in interpreting the experimental data obtained in this investigation are presented. The experimental results of ϕ of nitrogen, two mixtures of methane and carbon dioxide, two mixtures of methane, carbon dioxide and ethane, one mixture of methane, carbon dioxide and nitrogen, and a mixture of methane, carbon dioxide, nitrogen and ethane at various temperatures are also presented.

Procedure of the Experimental Measurements

The fluid under study was brought to the desired state of pressure and temperature at the inlet to the calorimeter with the recycle system shown in Figure 3. A pressure drop of 60 to 250 psi was obtained by adjustment of the flow of fluid through the calorimeter section. The flow rate was adjusted by control valve JTCV, manipulated manually. The voltage supplied to the calorimeter heater wire was adjusted manually until the temperature difference between the inlet and outlet of the calorimeter, indicated by the differential thermopiles was less than two microvolts (0.01°C). When steady state was reached, as indicated by the constancy of the pressure drop and the zero temperature difference across the calorimeter, the values of the variables were recorded. The time of approach to steady state was of the order of half to one hour.

Materials Used

The source and purity of the gases used in this work are given in Table II. The gases were used without further purification.

TABLE II

Materials

Component	Supplier	Purity
Nitrogen	Consumer's Welding Co.	99.993%
Methane	Matheson Gas Products	99.97 %
Carbon dioxide	Canadian Liquid Air Co. Ltd.	99.95 %
Ethane	Matheson Gas Products	99.96 %

Composition Determination

The composition of the mixtures in this study was determined chromatographically. The calibrations for the gas chromatograph are presented in Appendix A. The precision of the composition determinations was approximately ±0.2 mole percent as was checked by making several runs for each isotherm.

Interpretation of Data

The basic data were recorded in terms of quantities that can be readily measured, such as microvolts and height of a fluid. These quantities were converted to temperature, pressure, pressure drop, power input and flow rate. In the single phase region, the isothermal throttling coefficient ϕ which is shown in Equation (7) is obtained from the integral data by several techniques. Both graphical and computer reduction methods were used.

Graphical Interpretation

One may consider determining ϕ at constant temperature as a function of pressure. The experimental data were reported as sets of T, P_1, P_2 and $(\underline{H}_{P_2} - \underline{H}_{P_1})$ over a wide range of temperature. For any one data point,

$$\underline{H}_{P_2,T} - \underline{H}_{P_1,T} = \int_{P_1}^{P_2} \phi dP \tag{19}$$

or

$$\frac{\underline{H}_{P_2,T} - \underline{H}_{P_1,T}}{P_2 - P_1} = \phi_{T_m} = \frac{\int_{P_1}^{P_2} \phi dP}{P_2 - P_1} \tag{20}$$

where ϕ_{T_m} is the mean isothermal throttling coefficient between P_1 and P_2. Values of ϕ_{T_m} were plotted as horizontal lines are shown in Figures 5 and 10. The smooth ϕ_{T_m} curve was obtained by satisfying Equation (19): the area under the horizontal line segments, $\phi_{T_m} * (P_2 - P_1)$, should equal the area under the smooth isothermal throttling coefficient curve.

Computer Reduction

The above graphical procedures are extremely time consuming and in addition the equal area construction can easily lead to errors. Therefore, a computer program was developed for interpretation of integral data. The true isothermal throttling coefficient is given by,

$$\phi \equiv \lim_{\Delta P \to 0} \frac{q}{\Delta P} \equiv \left(\frac{\partial H}{\partial P}\right)_T$$

where $q = \frac{\dot{W}}{F}$ is the rate of electrical energy transfer per unit mass flow rate. The result of actual measurements is the mean ϕ, $\phi_m = q/(P_2 - P_1)$, associated with the mean pressure of the interval, $P_m = (P_1 + P_2)/2$. Deviation from linearity of the ϕ versus P curve will therefore require adjustment of the mean isothermal throttling coefficient by a curvature correction to yield the true isothermal throttling coefficient at P_m.

The curvature correction can be determined by considering the isothermal throttling coefficient to be represented by a cubic equation in pressure over a limited range

$$\phi = a_0 + a_1 P + a_2 P^2 + a_3 P^3 \qquad (21)$$

then

$$q = \int_{P_1}^{P_2} \phi \, dP$$

$$= a_0(P_2 - P_1) + \frac{a_1}{2}(P_2^2 - P_1^2) + \frac{a_2}{3}(P_2^3 - P_1^3) + \frac{a_3}{4}(P_2^4 - P_1^4) \quad (22)$$

and the mean ϕ is,

$$\phi_m = \frac{q}{P_2 - P_1}$$

$$= a_0 + \frac{a_1}{2}(P_2 + P_1) + \frac{a_2}{3}(P_2^2 + P_2P_1 + P_1^2)$$

$$+ \frac{a_3}{4}(P_2^3 + P_2^2P_1 + P_2P_1^2 + P_1^3) \quad (23)$$

The difference between the true ϕ and the mean ϕ_m at P_m is,

$$\phi - \phi_m = \frac{-(P_2 - P_1)^2}{24}[2a_2 + 3a_3(P_2 + P_1)] \quad (24)$$

Since at the mean pressure,

$$(\frac{\partial^2\phi}{\partial P^2}) = 2a_2 + 3a_3(P_1 + P_2) \quad (25)$$

the true isothermal throttling coefficient is,

$$\phi = \phi_m - \frac{(P_2 - P_1)^2}{24}(\frac{\partial^2\phi}{\partial P^2})_T \quad (26)$$

values of $(\frac{\partial^2\phi}{\partial P^2})_T$ were obtained by considering the mean isothermal to be sufficiently close to the true isothermal throttling coefficient and differentiating the smooth mean isothermal throttling coefficient.

The extended spline fit technique was used to obtain a smooth mean isothermal throttling coefficient and its second derivative with respect to P.

The Extended Spline Fit Method

The spline fit technique has been discussed by Landis and Nilson [41]. This method puts a different cubic between every two

successive data points such that the curve passes exactly through each data point and that the first two derivatives of the curve on the right hand side of the data point are equal, respectively, to the first two derivatives of the curve on the left hand side of the data point, all derivatives evaluated at the data point.

If, instead of defining the interval boundaries to pass through every data point, interval boundaries are determined arbitrarily such that each interval may contain a number of data points, the method can be extended to provide smoothing of the data. The details of this method are discussed by Klaus and Van Ness [39].

Extension to Low Pressure

Since the lower limit in pressure of the recycle flow system is 200 psia, data from the literature are used in extending the enthalpy results to zero pressure. The experimental isothermal throttling coefficients obtained at elevated pressures should extrapolate to the zero pressure values derived from the experimental second virial coefficients using Equation (14). The resulting curve was integrated to determine the effect of pressure on enthalpy at low pressures.

Experimental Results With Nitrogen

The experimental data were taken for nitrogen on the isothermal throttling calorimeter at four different temperatures from 273.15 to 374.15 K, and the pressure up to 2400 psia. Figure 5 shows the isothermal throttling coefficient, ϕ at 273.15 K plotted as a function of pressure. An equal area curve passing through the bars obtained point values of ϕ. The agreement between this work and Mather[57] is less than 1.0%. Figure 6 and 7 show the comparison of two different temperatures with other experimental results. The experimental band indicates the precision of about ±1/2% for this experiment. The data of Ishkin and Kaganer[33] are believed to be high by as much as 5% (see Mather[58]).

The values of ϕ can be calculated from an equation of state using Equation (8). The Benedict-Webb-Rubin[6] equation is frequently used for calculation of thermodynamic properties. For nitrogen, two sets of constants for this equation are available, those of Stotler and Benedict[83] and those of Bloomer and Rao[12]. Isothermal throttling coefficients were also calculated from the equation of state for nitrogen from the U.S. Bureau of Mines[93]. The results of equation of state calculation were compared with the experimental data in Figure 8 and 9.

Table III presents the smoothed experimental measurements of ϕ by this work.

Enthalpy departures were calculated from the experimental data by integration of ϕ with respect to pressure. The results for the three isotherms of this work were compared with other experimental calorimetric results in Table IV. The present data were in very good agreement with the most recent experimental values in the literature.

TABLE III

ISOTHERMAL THROTTLING COEFFICIENTS FOR NITROGEN

$-\phi$ (J mol^{-1} bar^{-1})

PRESSURE	Temperature, °C			
(bar)	0	30	70.3	101
0*	7.48	5.93	4.58	3.62
10	7.33	5.83	4.44	3.51
20	7.17	5.69	4.30	3.40
30	7.03	5.54	4.16	3.29
40	6.86	5.39	4.01	3.17
50	6.66	5.21	3.87	3.04
60	6.46	5.04	3.72	2.92
70	6.26	4.89	3.58	2.81
80	6.06	4.73	3.43	2.71
90	5.85	4.55	3.31	2.60
100	5.63	4.37	3.18	2.48
110	5.39	4.20	3.05	2.37
120	5.14	4.01	2.91	2.26
130	4.88	3.83	2.79	2.14
140	4.75	3.65	2.67	2.04
150	4.34	3.46	2.55	1.93
160	4.07	3.27	2.42	1.82

* $B - T\frac{dB}{dT}$

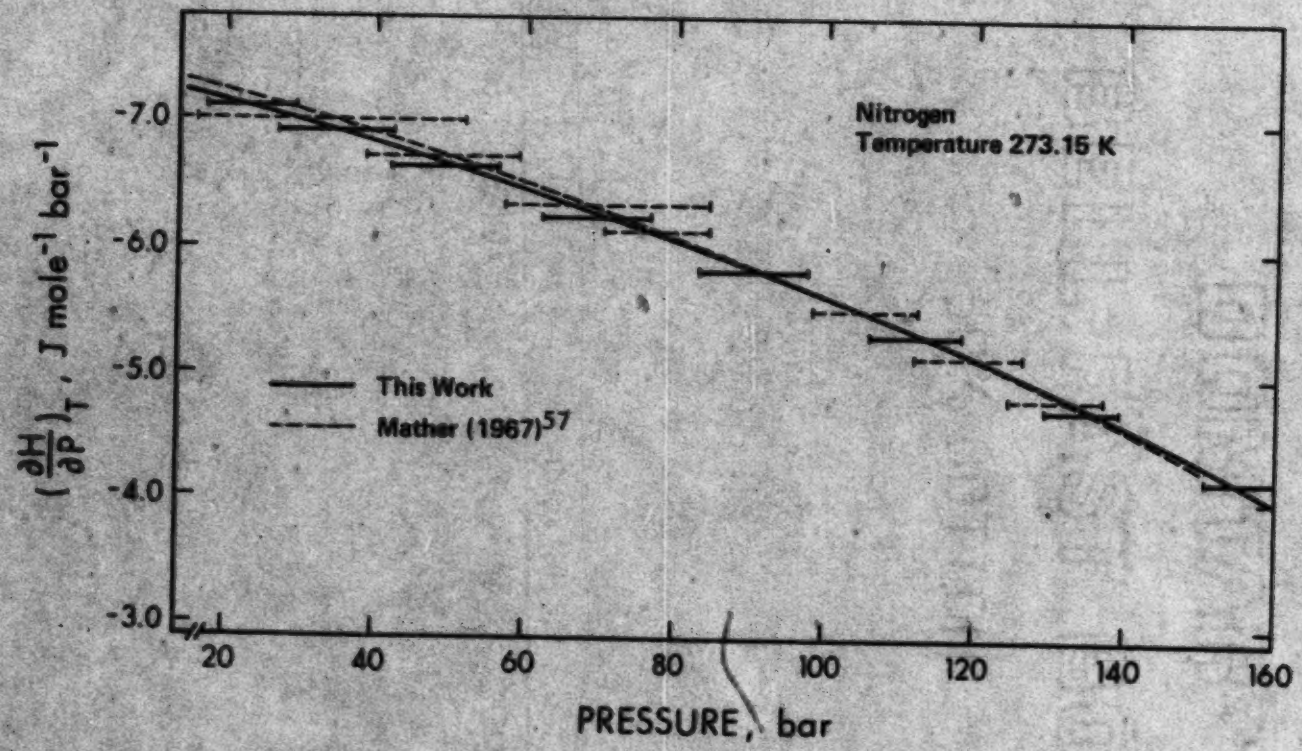


FIGURE 5. Isothermal Data on Nitrogen at 273.15 K

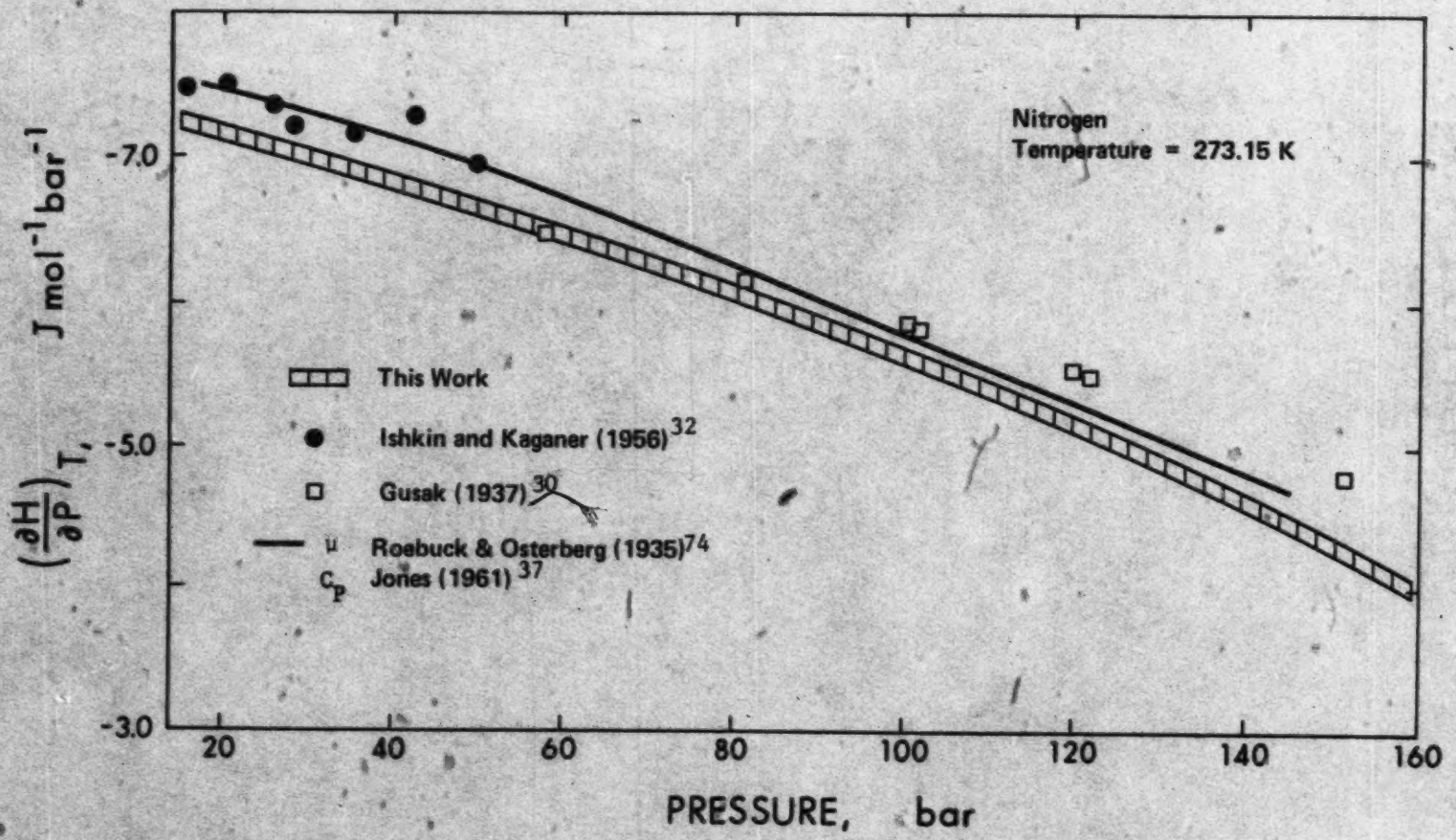


FIGURE 6. Comparison of Isothermal Data of Nitrogen With Other Experimental Data at 273.15 K

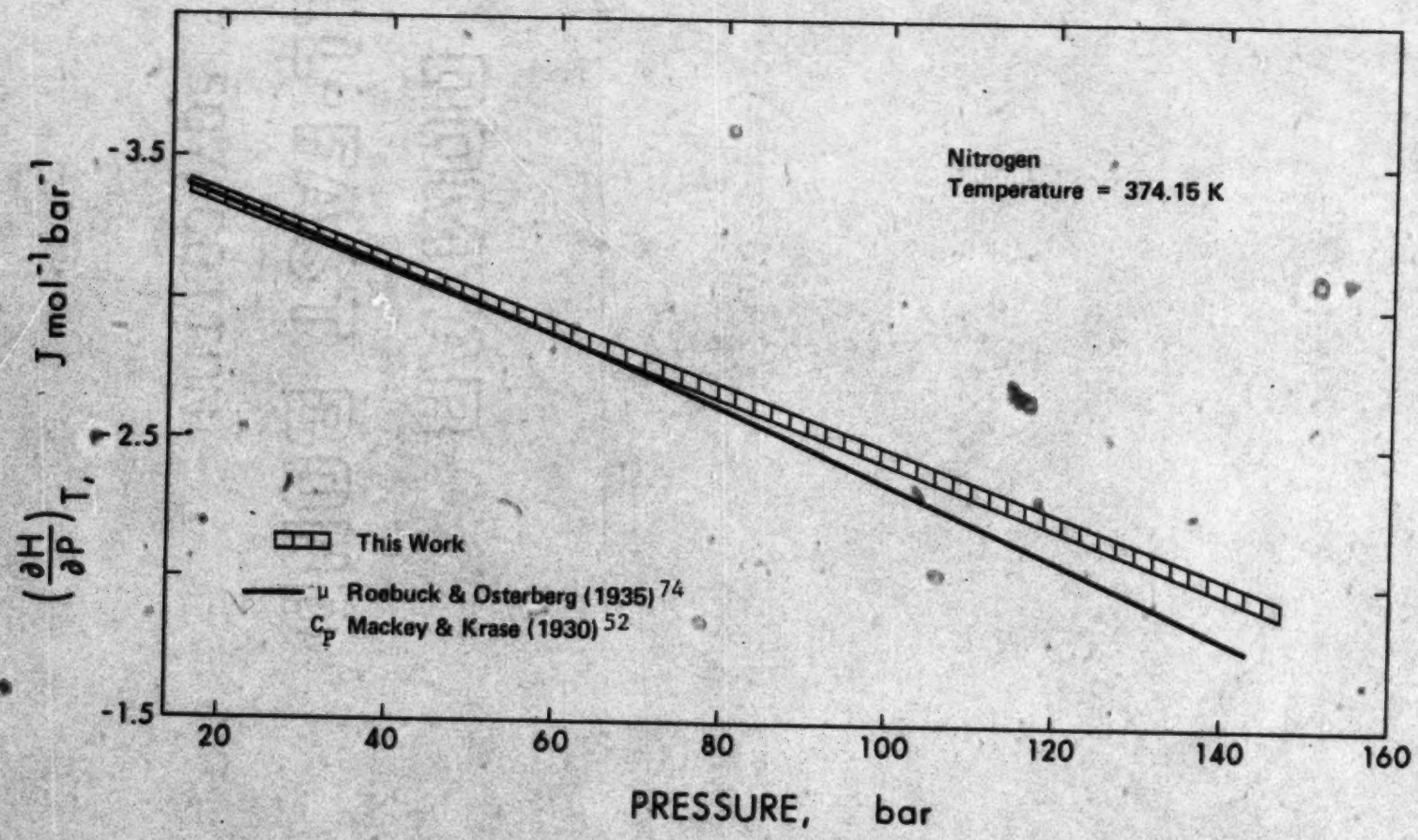


FIGURE 7. Comparison of ϕ of Nitrogen With Other Experimental Data at 374.15 K

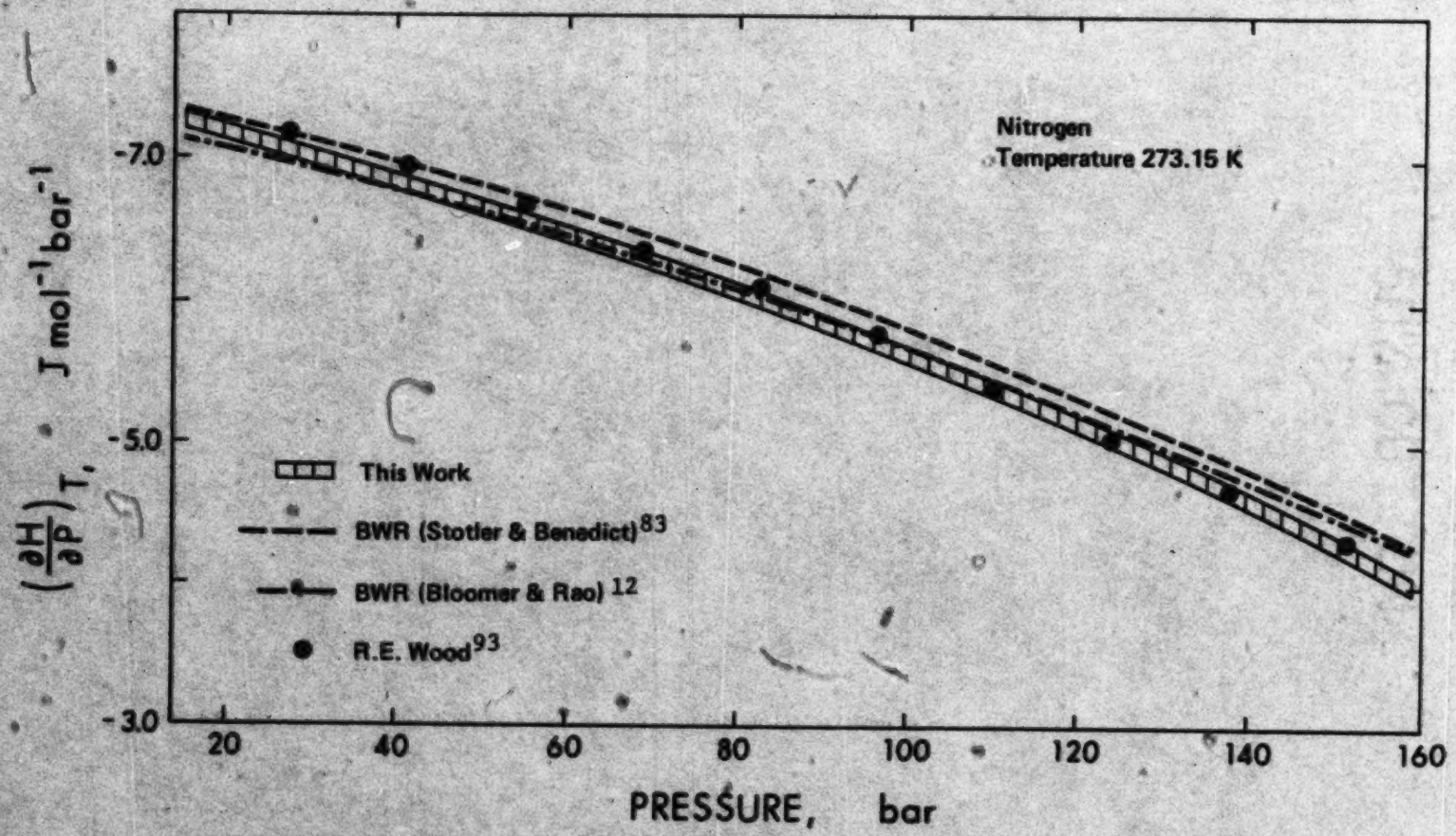


FIGURE 8. Comparison of Isothermal Data of Nitrogen with Values Predicted from Equations of State

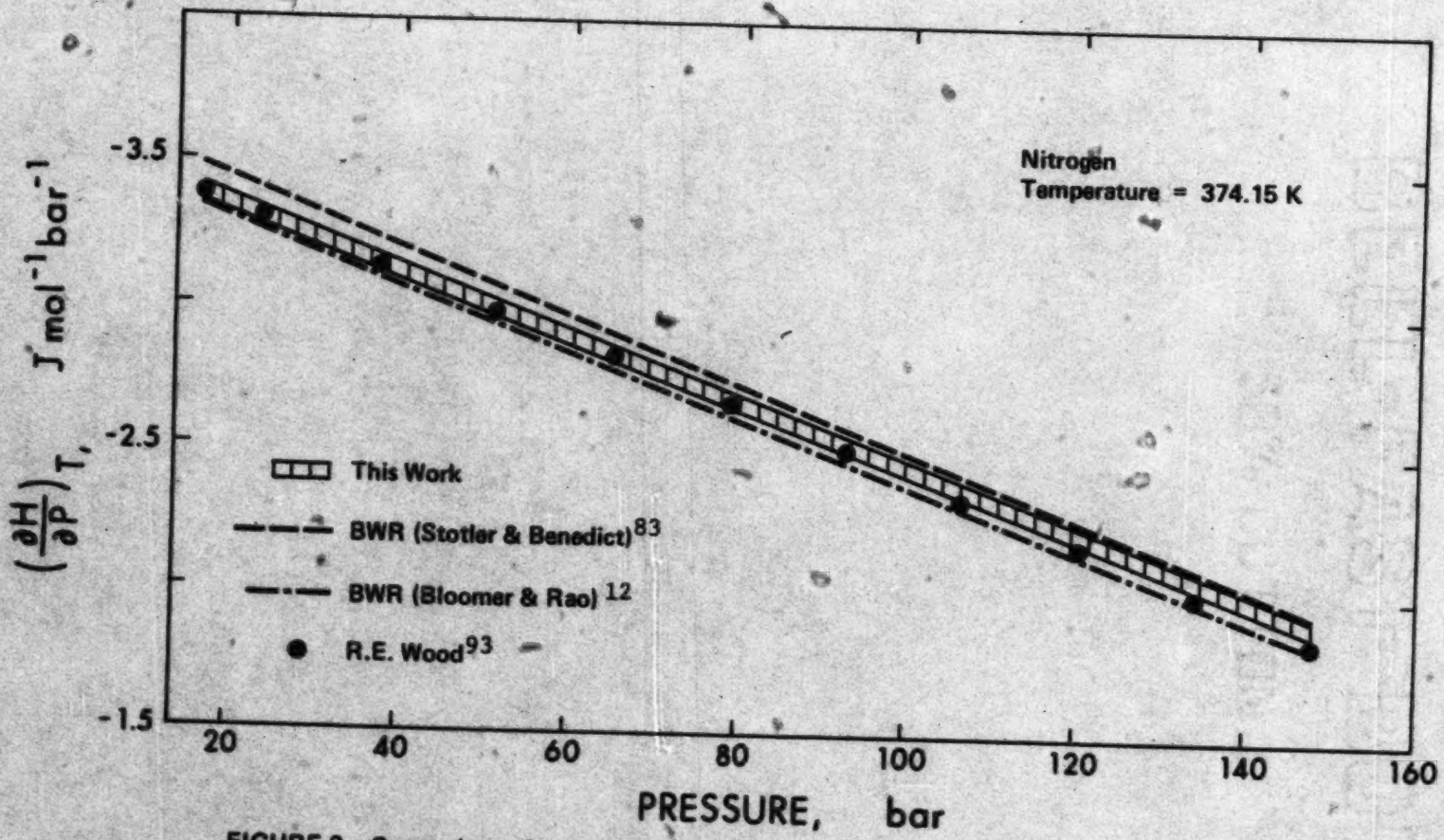


FIGURE 9. Comparison of Isothermal Data of Nitrogen with Values Predicted from Equations of State

TABLE IV

COMPARISON OF EXPERIMENTAL ENTHALPY DEPARTURES

FOR NITROGEN WITH OTHER EXPERIMENTAL WORKS

TEMPERATURE (K)	PRESSURE (bar)	$(H_o-H_p)_T$, J mol^{-1} This Work	Mather[57]	Dawe & Snowdon[21]
273.15	20	146.6	147	148
	40	287.0	290	291
	60	420.2	422	428
	80	545.4	543	558
	100	662.4	660	679
303.15	20	116.4	-	117
	40	227.2	-	230
	60	331.5	-	338
	80	429.2	-	439
	100	520.2	-	532
374.15	20	70.2	-	67
	40	136.0	-	132
	60	196.8	-	194
	80	253.1	-	252
	100	305.0	-	305

Experimental Results With Methane - Carbon Dioxide Mixtures

The measurements of the isothermal throttling coefficient were made on 42.3 mole percent of methane in carbon dioxide at four isotherms, 0, 40, 60 and 90°C. The pressure ranged from 400 to 2000 psia. Measurements were also made at six isotherms and the same pressure range for 14.5 mole percent of methane in carbon dioxide. The six isotherms were 0, 10, 20, 40, 60 and 90°C.

Typical isothermal data are presented in Figure 10. Average values of $\phi_m = (\Delta H/\Delta P)_T$ were plotted as horizontal lines and the computer reduction method was used to determine point values of $\phi = f(P)$ as illustrated by the solid curve. In extrapolating the results of the experimental investigation to zero pressure, it was necessary to use Equation (14) for ϕ° in terms of second virial coefficient. Values of ϕ° were calculated from the virial coefficients given by Dymond and Smith[24] and Ng[63]. The calculation of ϕ° is shown in Appendix C.

Tables of ϕ values of all of the experimental isotherms are presented in Table V and VI. Figure 11 and 12 present the plot of ϕ as a function of temperature at different isobars for the two mixtures.

Comparison of Results

Since the isothermal experimental data on the carbon dioxide-methane mixtures with same compositions are not available in the literature, comparison cannot be made. However, the isothermal throttling coefficients of two mixtures at each isotherm and at a pressure up to 2000 psia can be calculated by using BWR equation of state and Bishnoi and Robinson[11] mixing rules. The parameters of carbon dioxide and methane, reported by Bishnoi and Robinson[10] were utilized in the above calculations.

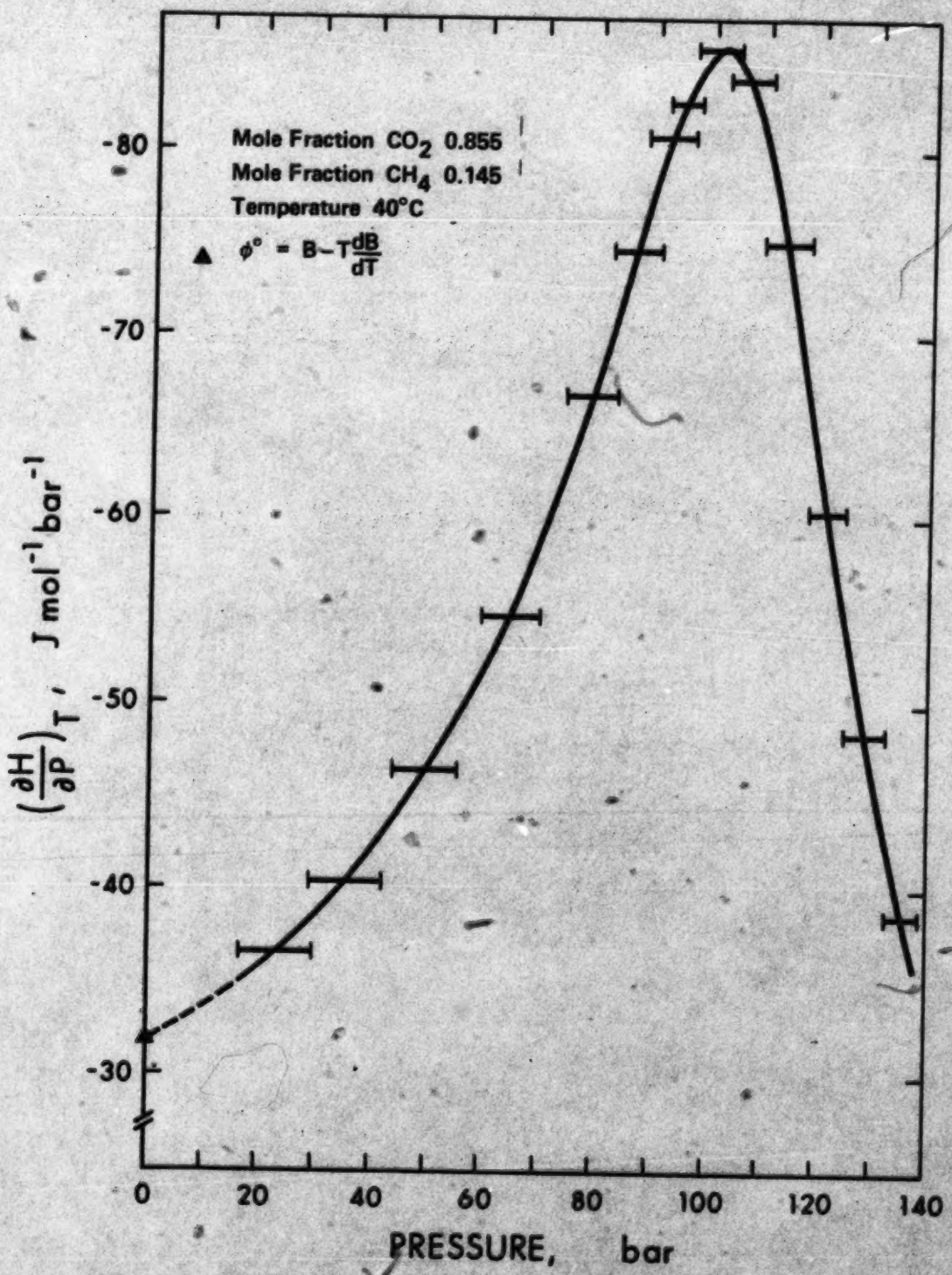


FIGURE 10. Isothermal Throttling Coefficient for the 14.5 percent CH_4 in CO_2 Mixture at 40°C

TABLE V

ISOTHERMAL THROTTLING COEFFICIENTS FOR

THE 42.3 MOLE PERCENT METHANE IN CARBON DIOXIDE

$-\phi$ (J mol^{-1} bar^{-1})

PRESSURE (bar)	Temperature °C 0	40	60	90
0*	32.46	24.10	21.30	18.20
10	34.42	24.95	21.92	18.48
20	37.10	25.95	22.58	18.78
30	40.70	27.09	23.28	19.05
40	45.41	28.27	23.95	19.32
50	52.15	29.48	24.60	19.58
60	62.04	30.76	25.20	19.83
70	74.71	32.05	25.76	20.01
80	87.75	33.24	26.27	20.13
90	85.77	34.23	26.69	20.17
100	63.71	34.90	26.95	20.17
110	43.52	34.97	27.00	20.12
120	30.04	34.11	26.76	20.00
130	21.55	32.27	26.17	19.74
137	17.75	31.19	25.53	19.43

* $B - T\frac{dB}{dT}$

TABLE VI

ISOTHERMAL THROTTLING COEFFICIENTS FOR

THE 14.5 MOLE PERCENT METHANE IN CARBON DIOXIDE

$-\phi$ (J mol^{-1} bar^{-1})

PRESSURE (bar)	Temperature, °C 0	10	20	40	60	90
0*	44.23	40.92	36.79	31.91	27.78	23.81
10	49.61	45.64	39.89	33.48	29.18	24.35
20	57.46	51.80	43.82	35.55	30.67	24.97
30	69.86	60.15	48.57	38.28	32.19	25.67
40	-	73.79	54.82	42.13	35.97	26.54
50	-	96.73	67.63	46.32	36.04	27.42
60	-	-	90.03	51.54	38.37	28.30
70	-	-	129.5	58.39	40.92	29.16
80	9.99	-	241.8	67.48	43.66	30.00
90	7.61	20.90	99.40	78.06	46.53	30.80
100	6.10	14.21	44.51	85.15	49.17	31.48
110	5.02	10.78	25.76	80.53	50.91	31.94
120	3.98	8.43	17.96	63.06	51.07	32.16
130	-	7.06	14.65	46.30	49.11	32.18
137	-	6.38	11.54	37.00	46.37	32.11

* $B - T\frac{dB}{dT}$

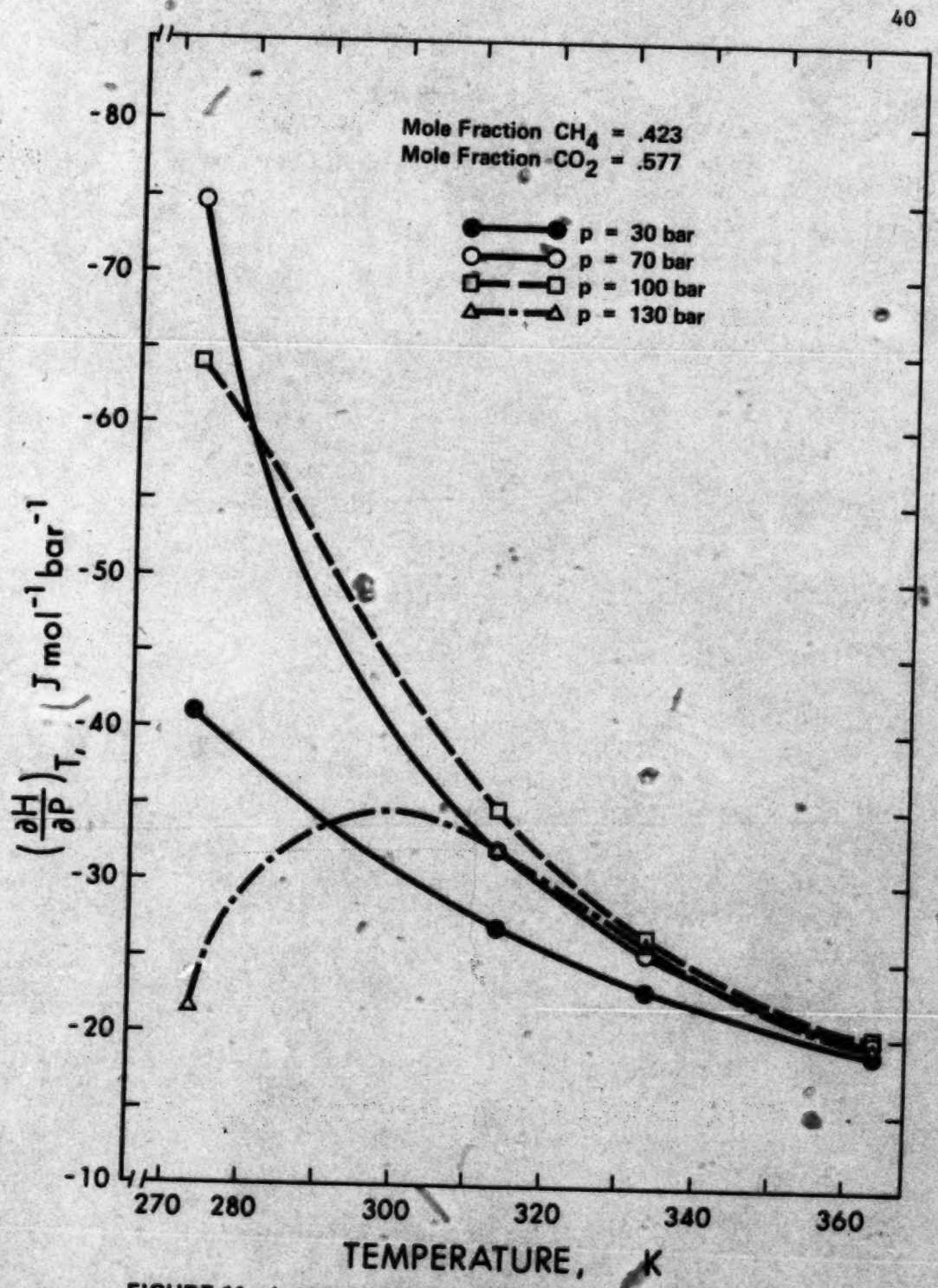


FIGURE 11. Isothermal Throttling Coefficient for the 42.3 percent CH_4 in CO_2 Mixture at Various Constant Pressures

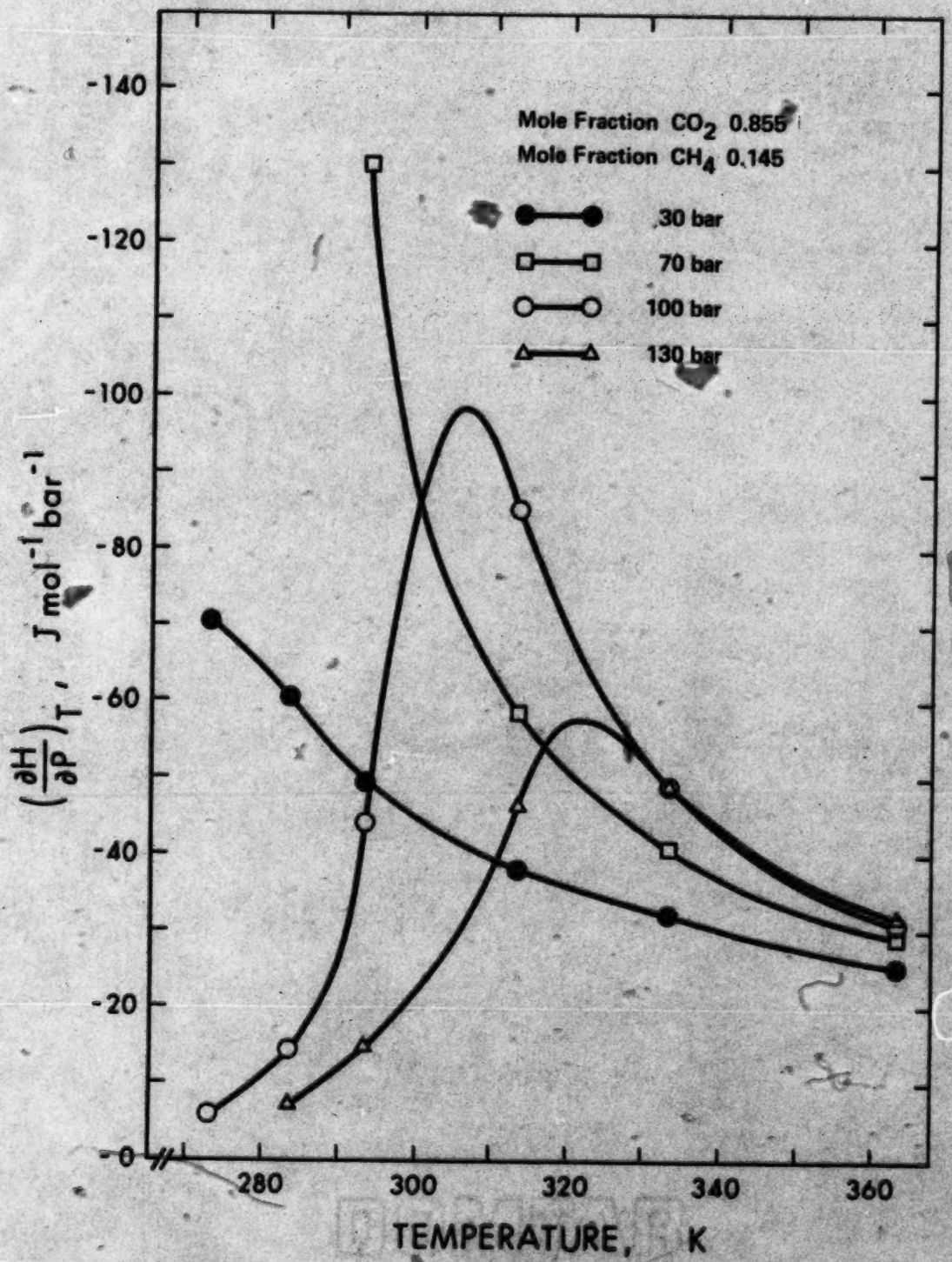


FIGURE 12. Isothermal Throttling Coefficient for the 14.5 percent CH_4 in CO_2 Mixture at Various Constant Pressures

In general, the deviations are larger at the lower pressures of the lower temperature. The comparison of the experimental data and the calculated values from BWR equation of state for 42.3 percent methane in carbon dioxide at 0°C and 14.5% mixture at 90°C are shown in Figure 13 and 14 respectively.

Peterson and Wilson[68] reported results of isothermal enthalpy departure from isothermal throttling experiments for equimolal methane-carbon dioxide mixture at pressure from 20 to 2000 psia and temperature from -50°F to 300°F. Isothermal enthalpy departures of the two mixtures of this work were calculated by integration with respect to pressure. The results were then interpolated to 100°F and 150°F at pressure of 800, 1200, 1600 and 2000 psia. The final results were plotted at constant pressure and temperature as a function of mole fraction. Enthalpy departure of pure methane and carbon dioxide were obtained from modified BWR equation proposed by Starling (BWRS)[50,78] with the parameters from Starling[80]. Figure 15 shows the comparison of the results between this work and that of Peterson and Wilson[68] at 100°F. The comparison at 150°F is also in good agreement.

Enthalpy Tables and Diagrams

The experimental data on the effect of pressure on enthalpy by this work and the effect of temperature on enthalpy by Bishnoi[9] for the methane - carbon dioxide mixtures have been used to prepare skeleton enthalpy tables and diagrams. Tables and diagrams are presented for 14.5 and 42.3 mole percent methane in carbon dioxide mixtures. Comparisons were made with excess enthalpy data from the literature.

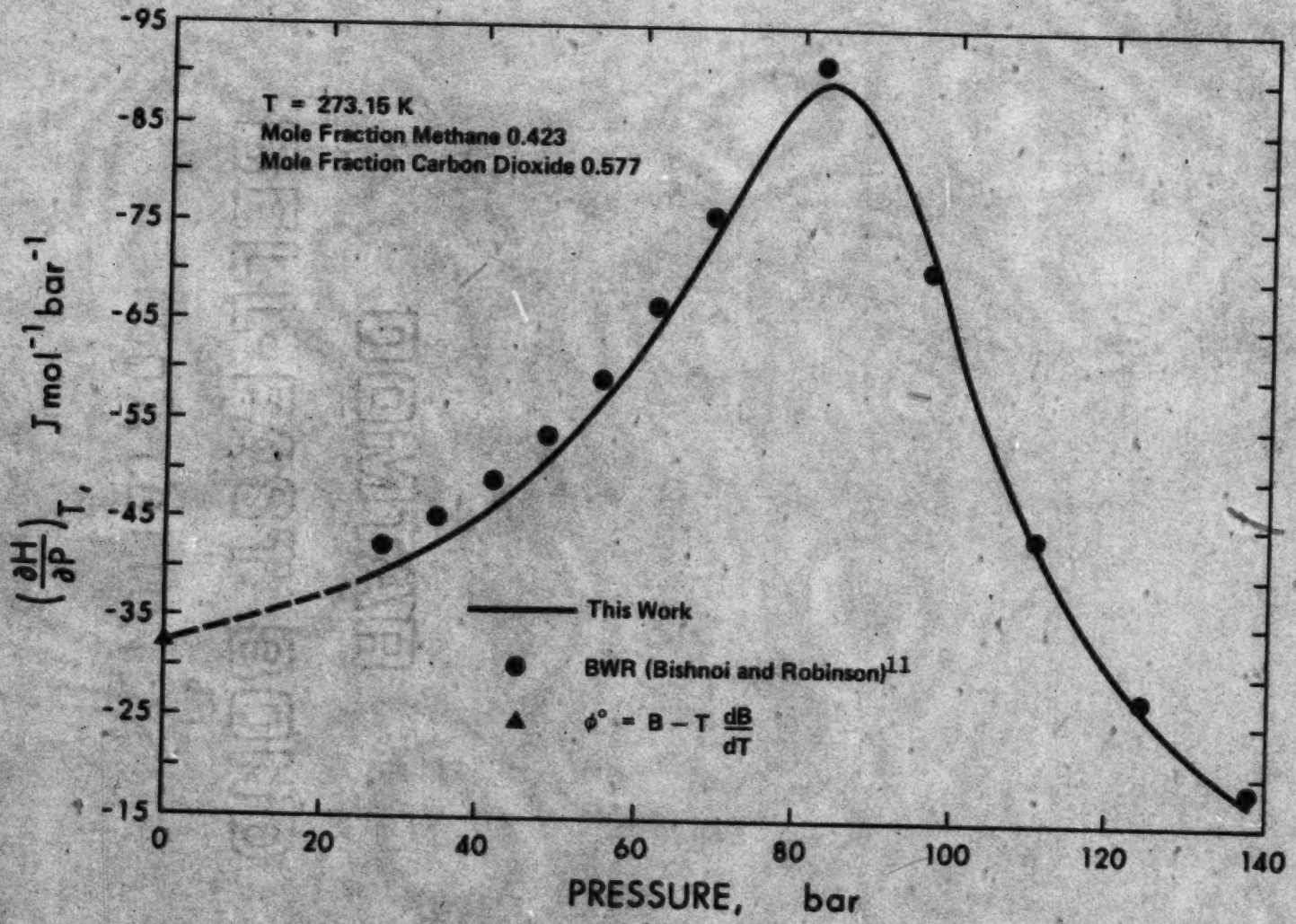


FIGURE 13. ϕ of 42.3 Mole Percent Mixture at 273.15 K

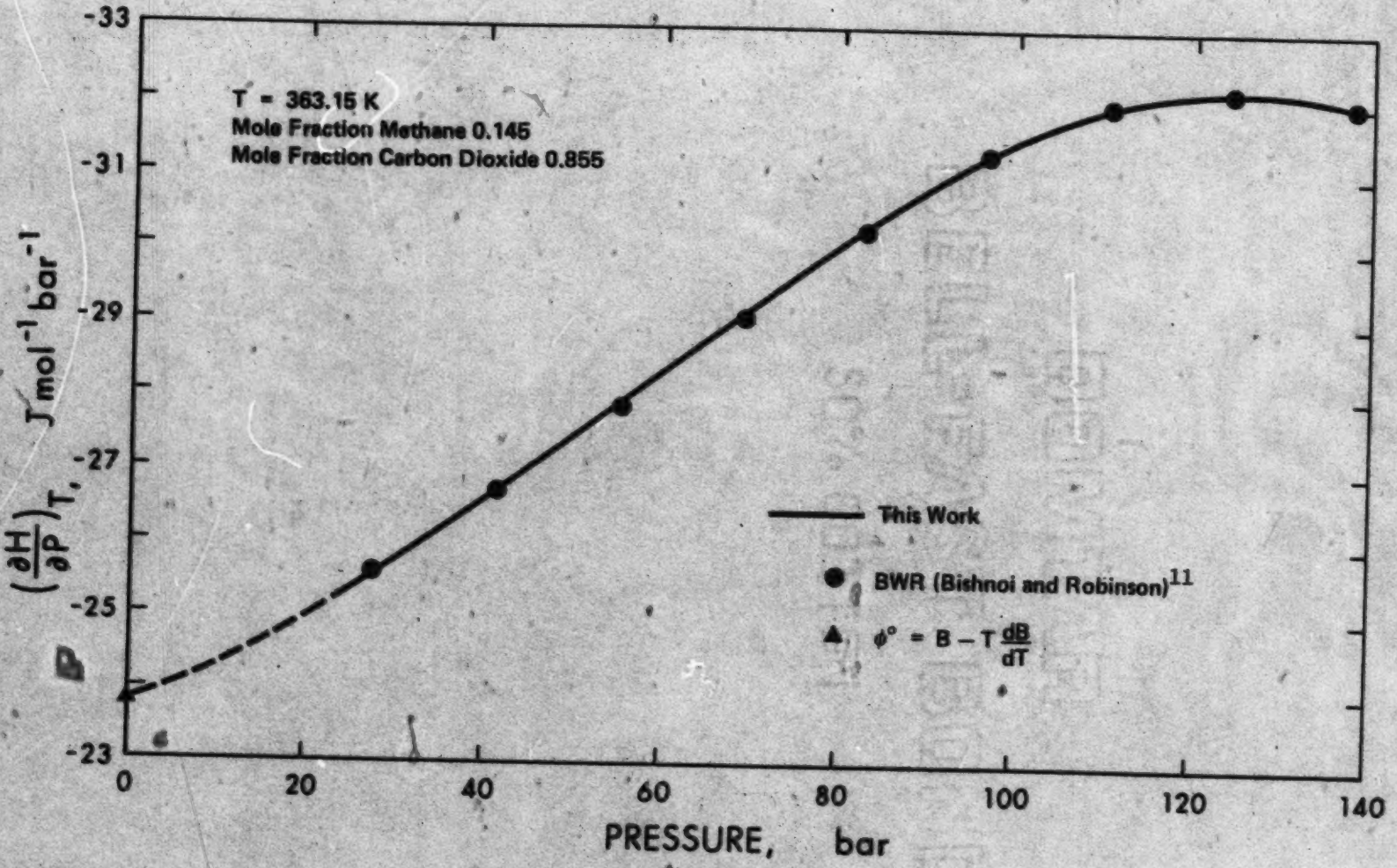


FIGURE 14. ϕ of 14.5 Mole Percent Mixture at 363.15 K

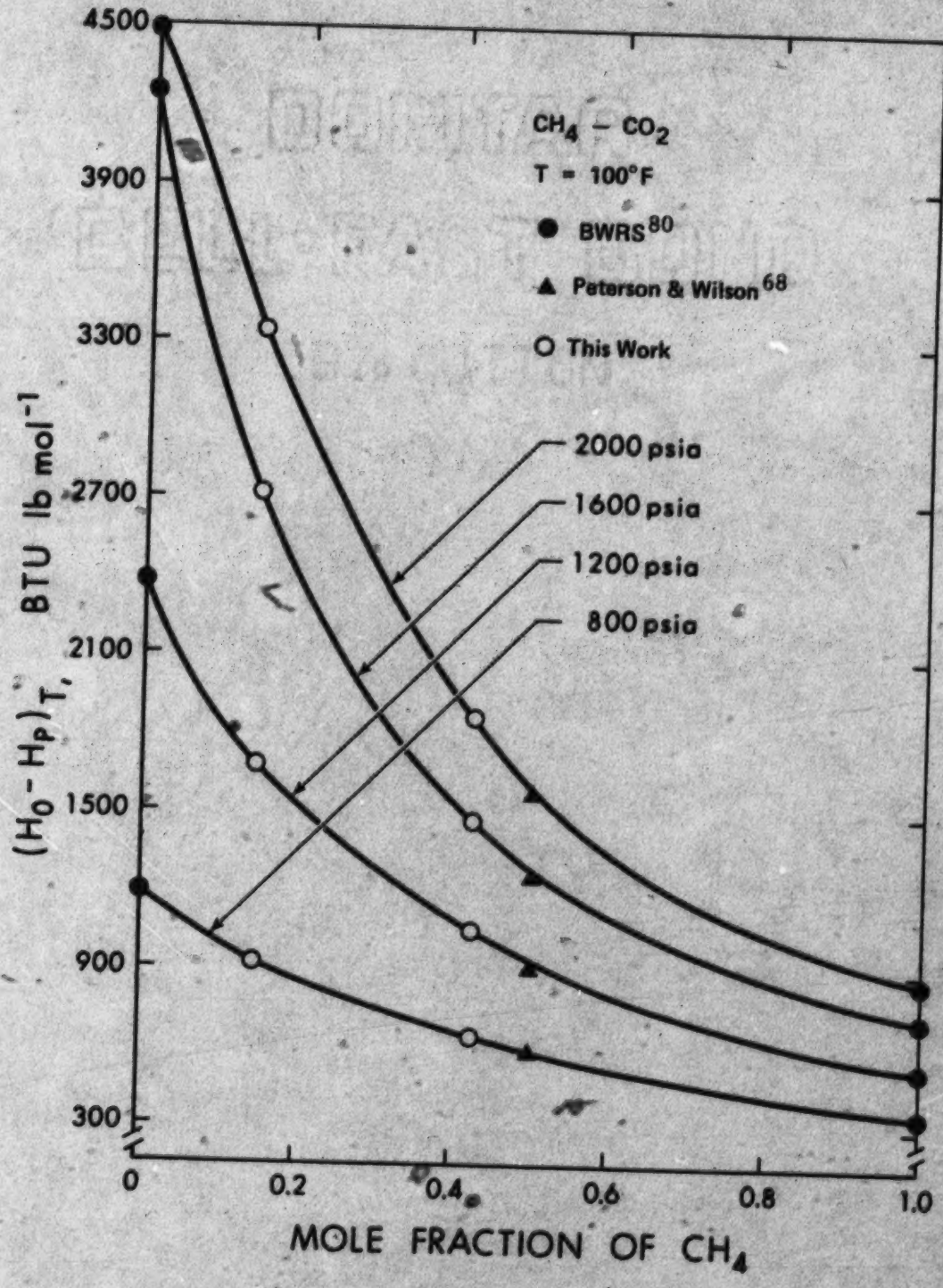


FIGURE 15. Enthalpy Departures for Mixtures of Methane and Carbon Dioxide

Nominal 14.5 Percent Methane in Carbon Dioxide Mixture

A skeleton enthalpy table and a pressure-enthalpy-temperature diagram for this mixture have been prepared which are based entirely on experimental calorimetric data. The following procedure was used in preparing the diagram and table:

1. Reference state of 0 J/mole were taken to be the pure components as perfect crystals under zero pressure at absolute zero temperature.
2. The enthalpy of pure methane as a gas at zero pressure and 0 K was calculated using the enthalpy of methane (saturated vapor) at 100 K reported by Din[23], the B-W-R equation of state with parameters from Bishnoi and Robinson[10] to correct from 0.344 atm to zero pressure, and value of the ideal gas enthalpies from McBride et al.[61], the following results were obtained:

	$kJ\ mol^{-1}$
Enthalpy of methane at 100 K and 0.344 atm	+12.4775
Corrected to ideal gas (0.344 to 0 atm)	+ 0.05535
Ideal gas enthalpy change from 100 to 0 K	- 3.3126
	9.22025

so, the enthalpy of pure methane from perfect crystal at 0 K to any temperature at zero pressure is,

$$H_T = 9.22025 + (H_T^\circ - H_o^\circ)\ kJ\ mol^{-1}$$

where $(H_T^\circ - H_o^\circ)$ is the ideal gas enthalpy change reported by

McBride et al.[61].

3. The enthalpy of pure carbon dioxide as a gas at zero pressure and any temperature is reported by Vukalovich and Altunin[85] as follows:

$$H_T = 26.2235 + (H_T^\circ - H_o^\circ) \quad kJ\ mol^{-1}$$

where $(H_T^\circ - H_o^\circ)$ is the ideal gas enthalpy change reported by McBride et al.[61].

4. The enthalpy of methane-carbon dioxide mixture at zero pressure and any temperature T K was calculated assuming zero heat of mixing under these conditions.

$$H_{T,mix} = \sum_i x_i H_{T,i}$$

$$= 23.7580 + 0.145(H_T^\circ - H_o^\circ)_{CH_4} + 0.855(H_T^\circ - H_o^\circ)_{CO_2} \quad kJ\ mol^{-1}$$

5. The isothermal effect of pressure on enthalpy at 293.15, 313.15, 333.15 and 363.15 K was obtained from the integral ϕ data of this work from 0 to 138 bar. For temperatures at 283.15 and 273.15 K, the isothermal effect of pressure on enthalpy was obtained from 0 to 35 bar. The enthalpy departures for this mixture are presented as function of temperature in Figure 16 and comparison is made with values calculated from equations of state. BWR equation with Bishnoi and Robinson[11] mixing rules predicts higher departures, while Soave-Redlich-Kwong[76] equation with the interaction constant k_{ij} from Peng[66] is seen to predict lower departures. BWRS equation with parameters of Hopke and Lin[32] gives better predictions.

6. The isobaric heat capacity data of Bishnoi[9], at 312.86, 333.71, 363.6 and 423.75 K was used to determine the isobaric effect of

temperature on enthalpy. Since enthalpy is a property, changes in enthalpy are independent of the path chosen and the consistency of the experimental data can be tested by making loop checks. A grid consisting of 8 loops which is shown in Figure 34 was constructed and the enthalpy change around each loop evaluated. The actual sum divided by the sum of the absolute values of the enthalpy differences in the loop,

$$\% \text{ deviation} = \frac{\sum_i \Delta H_i}{\sum_i |\Delta H_i|} \times 100 \qquad (27)$$

provides a good measure of the consistency of the data[8]. The maximum percentage deviation of each loop is less than 0.37 percent and the percentage deviation of each loop is shown in Table XXVII.

Adjustments were made on individual values of ΔH_i as required to make $\sum_i \Delta H_i = 0$ for all loops. These adjustments were made within the limits of precision of the basic data. The accuracy of the heat capacity data is within ±0.5%[10]. Error analysis of this work is presented in Appendix A. The accuracy of the isothermal throttling coefficient is within ±1.0%. The amount of the adjustments are presented in Figure 34.

7. A smooth plot of the results was prepared and is shown in Figure 17. The values of enthalpy are given in Table VII.

Nominal 42.3 Percent Methane in Carbon Dioxide Mixture

A skeleton enthalpy table and a pressure-enthalpy diagram for this mixture have been prepared.

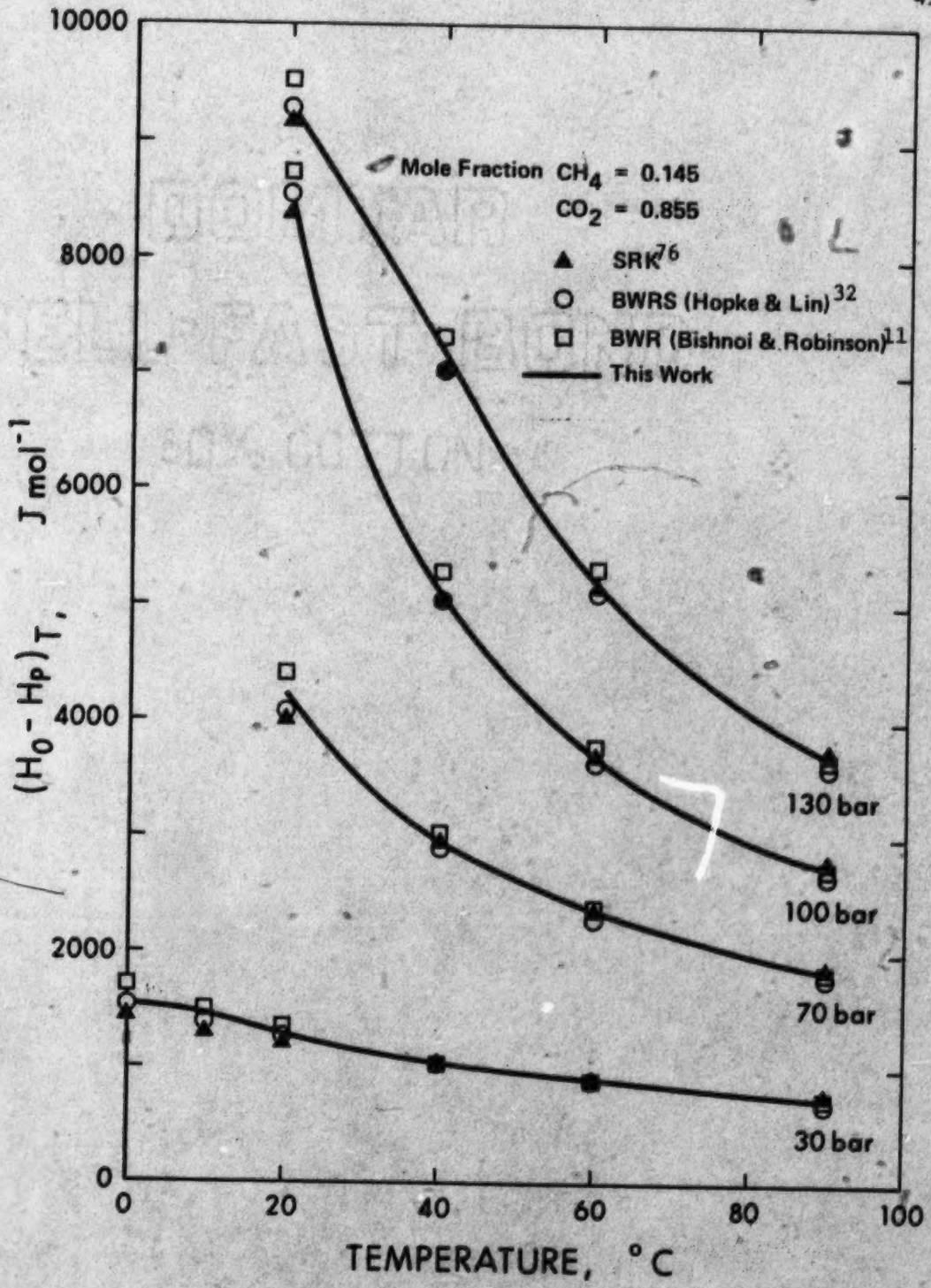


FIGURE 16. Enthalpy Departures for the 14.5 Percent Mixture

TABLE VII

Tabulated Values of Enthalpy for the
14.5 Percent of Methane in Carbon Dioxide

Datum: Pure crystal of $CH_4 + CO_2$ at 0 K and zero pressure

P bar \ T K	$H_{P,T} - H_{o,o}$ (kJ mol^{-1})								
	273.15	283.15	290	293.15	300	310	313.15	320	330
0.00	32.313	32.673	32.920	33.038	33.290	33.660	33.781	34.035	34.415
10.00	31.865	32.245	32.505	32.645	32.915	33.320	33.435	33.725	34.120
20.00	31.315	31.735	32.060	32.225	32.525	32.965	33.100	33.390	33.815
30.00	30.690	31.175	32.585	31.770	32.095	32.580	32.725	33.040	33.495
40.00	29.800	30.545	31.060	31.255	31.625	32.170	32.325	32.675	33.155
50.00		29.550	30.445	30.655	31.100	31.720	31.895	32.280	32.805
60.00			29.650	29.905	30.475	31.210	31.415	31.845	32.420
70.00			28.440	28.830	29.670	30.620	30.870	31.365	32.050
80.00			25.790	26.850	28.510	29.910	30.230	30.830	31.555
90.00			23.915	25.135	27.290	29.095	29.500	30.210	31.070
100.00			23.360	24.465	26.375	28.220	28.675	29.510	30.560
110.00				24.130	25.560	27.355	27.830	28.825	30.045
120.00				23.915	24.975	26.660	27.115	28.200	29.525
130.00				23.750	24.615	26.130	26.585	27.650	29.000
137.89				23.650	24.470	25.800	26.260	27.250	28.575

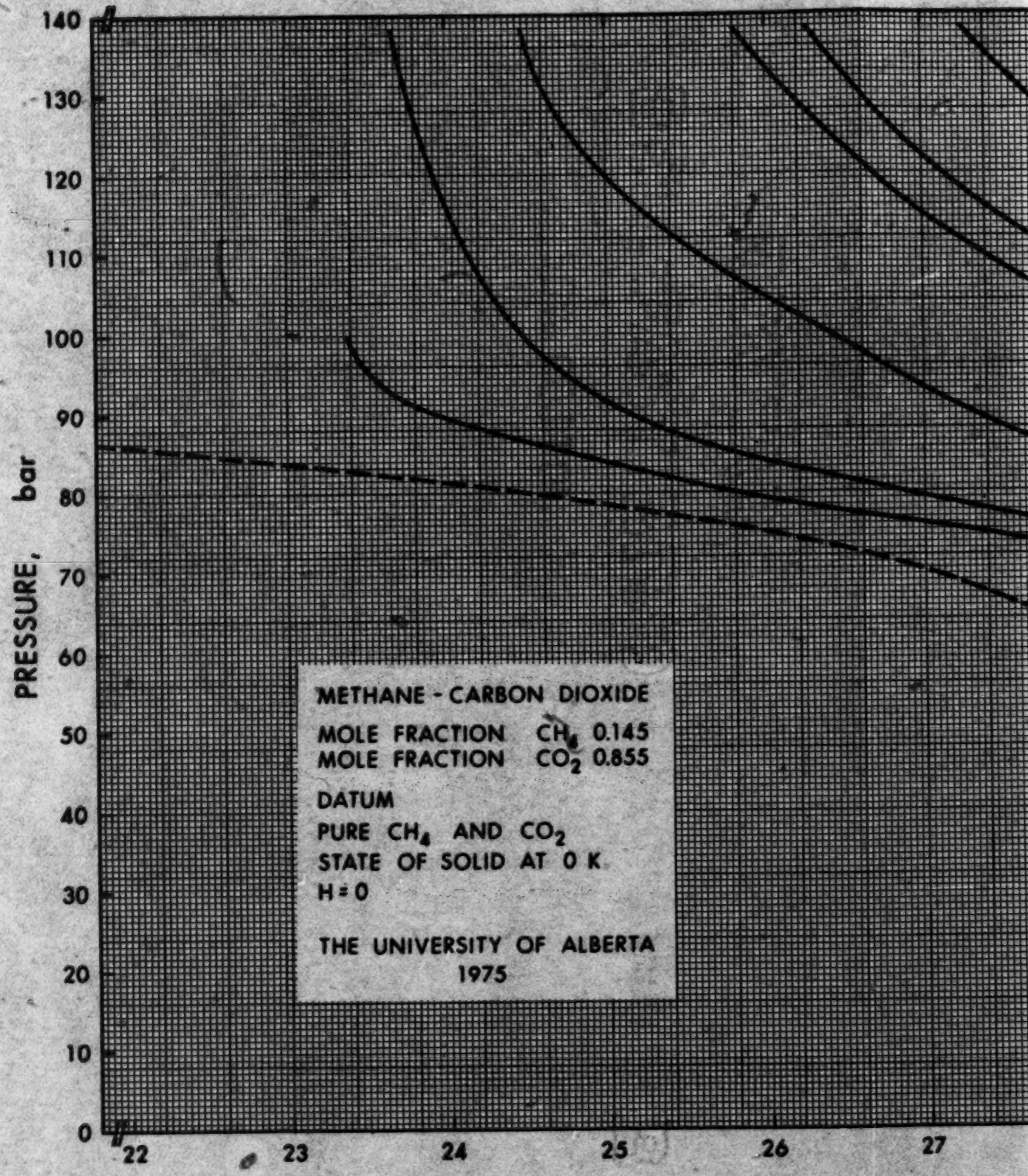
TABLE VII (continued)

CH_4(14.5%) - CO_2

P / bar \ T K	$H_{P,T} - H_{o,o}$ (kJ mol^{-1})							
	333.15	340	350	360	363.15	370	380	390
0	34.542	34.810	35.200	35.590	35.715	35.990	36.400	36.805
10.00	34.260	34.530	34.945	35.355	35.480	35.770	36.190	36.620
20.00	33.960	34.245	34.680	35.110	35.230	35.540	35.970	36.410
30.00	33.645	33.950	34.400	34.850	34.985	35.300	35.750	36.095
40.00	33.310	33.645	34.110	34.580	34.725	35.050	35.515	35.970
50.00	32.960	33.320	33.815	34.300	34.460	34.795	35.275	35.740
60.00	32.595	32.970	33.505	34.020	34.190	34.530	35.030	35.510
70.00	32.205	32.605	33.180	33.725	33.895	34.265	34.780	35.280
80.00	31.780	32.215	32.835	33.415	33.595	33.985	34.525	35.055
90.00	31.330	31.820	32.485	33.095	33.300	33.705	34.270	34.830
100.00	30.850	31.410	32.120	32.770	32.980	33.415	34.015	34.610
110.00	30.365	30.995	31.755	32.450	32.665	33.130	33.755	34.375
120.00	29.865	30.550	31.370	32.120	32.345	32.830	33.495	34.140
130.00	29.360	30.090	30.975	31.780	32.025	32.530	33.230	33.900
137.89	28.950	29.710	30.650	31.510	31.770	32.300	33.020	33.700

TABLE VII (continued)

P / bar \ T / K	$H_{P,T} - H_{o,o}$ (kJ mol^{-1})				
	400	410	420	423.15	430
0	37.220	37.620	38.030	38.173	38.440
10.00	37.040	37.460	37.860	38.000	38.285
20.00	36.850	37.285	37.685	37.830	38.125
30.00	36.655	37.095	37.515	37.660	37.970
40.00	36.445	36.900	37.345	37.490	37.800
50.00	36.230	36.710	37.170	37.320	37.625
60.00	36.020	36.510	36.995	37.145	37.450
70.00	35.805	36.315	36.815	36.975	37.290
80.00	35.595	36.120	36.630	36.800	37.115
90.00	35.390	35.930	36.450	36.620	36.950
100.00	35.190	35.735	36.270	36.445	36.780
110.00	34.975	35.540	36.090	36.270	36.610
120.00	34.755	35.335	35.910	36.085	36.440
130.00	34.530	35.135	35.720	35.900	36.270
137.89	34.345	34.965	35.560	35.747	36.130


PRESSURE, bar
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
22
23
24
25
26
27
METHANE - CARBON DIOXIDE
MOLE FRACTION CH_4 0.145
MOLE FRACTION CO_2 0.855
DATUM
PURE CH_4 AND CO_2
STATE OF SOLID AT 0 K
H = 0
THE UNIVERSITY OF ALBERTA
1975

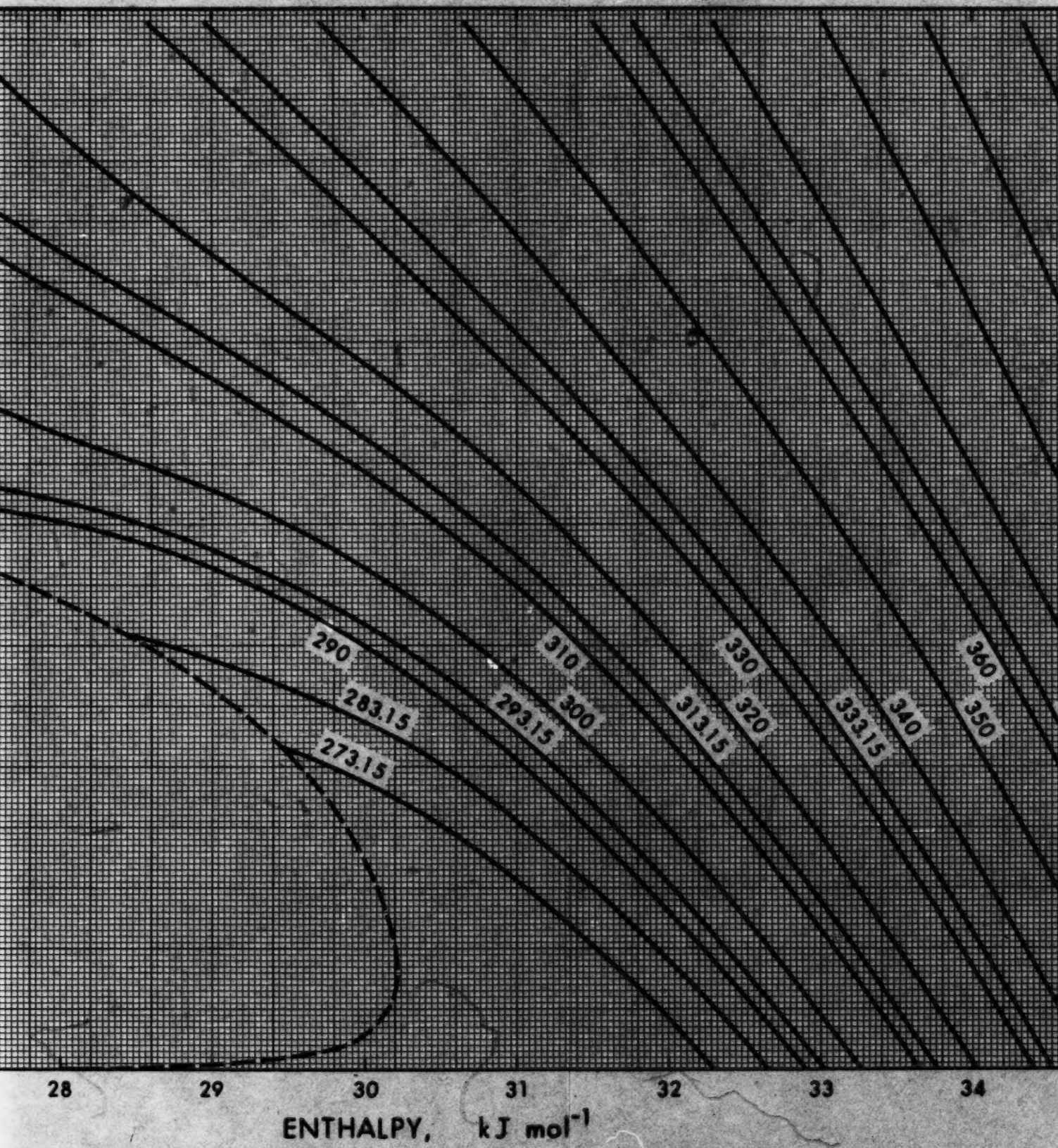
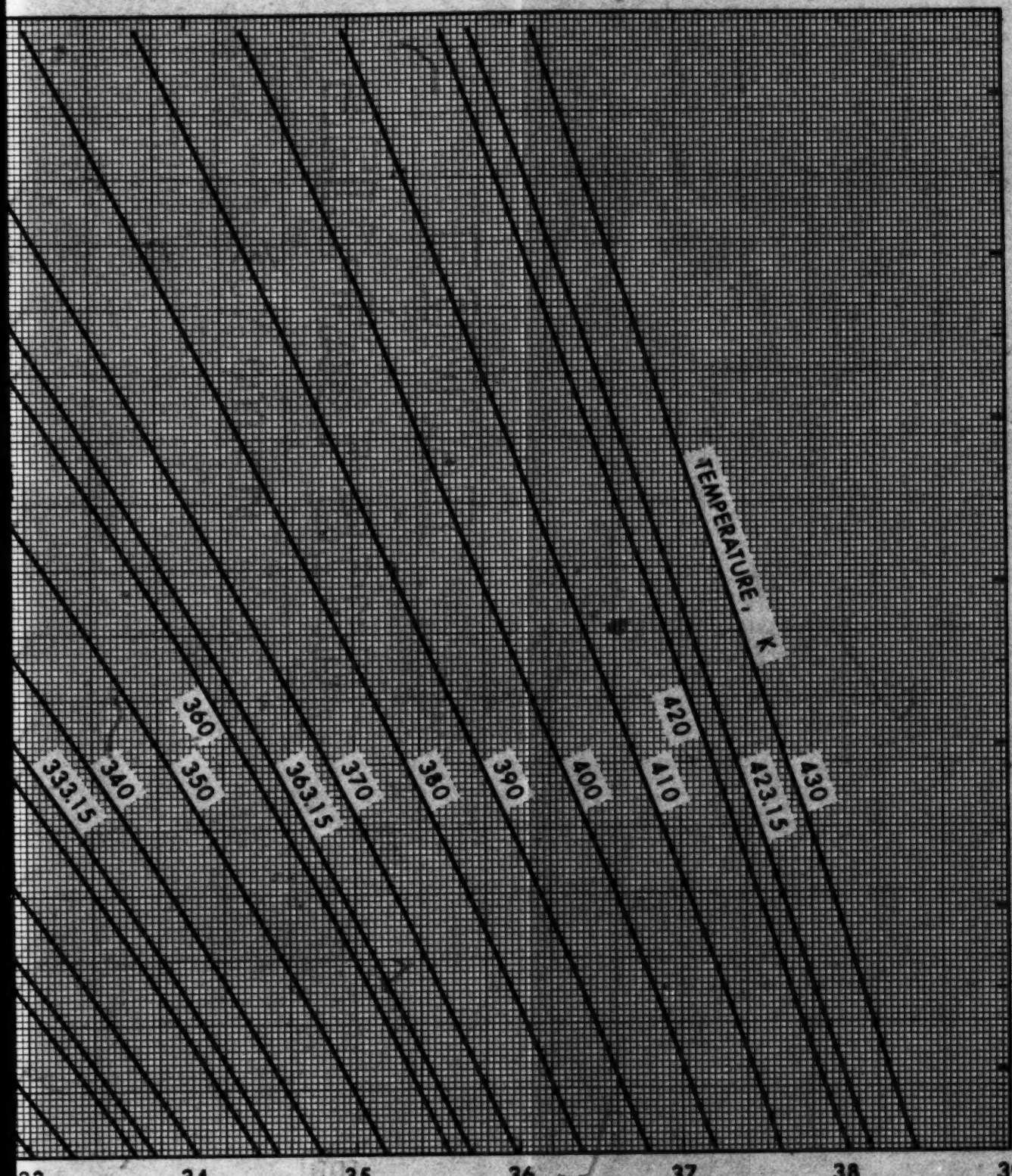


FIGURE 17. Pressure – Temperature – Enthalpy Diagram for 14.5 per cent of Methane in Carbon Dioxide



n Dioxide

343

The isothermal effect of pressure on enthalpy at 273.15, 313.15 and 333.15K was obtained from the integrated ϕ data of this work from 0 to 138 bar.

The isobaric heat capacity data of Bishnoi[9] at 313.07, 333.63 and 363.45K was used to determine the isobaric effect of temperature on enthalpy.

A grid consisting of 8 loops was constructed and enthalpy change around each loop evaluated. Figure 35 shows the location and enthalpy changes of the loops. In all closure the percentage deviation is less than 0.3 percent and the percentage deviation of each loop is shown in Table XXVIII.

Adjustments were made to make $\Sigma_i \Delta H_i = 0$ for all loops and the amount of adjustment is presented in Figure 35.

A smooth plot of the results was prepared and is shown in Figure 18. The values of enthalpy are given in Table VIII.

Comparison of Methane - Carbon Dioxide Mixtures Enthalpy Data

The heat of mixing or excess enthalpy for the two mixtures was calculated at various pressures from the data of Table VII and VIII together with the methane data of Din[23] and carbon dioxide data of Vukolovich et al.[85]. The results were compared with the excess enthalpy data of Lee and Mather[45] directly determined using a flow calorimeter. The comparison is shown in Figure 19 and 20. The agreement is generally good.

TABLE VIII

Tabulated Values of Enthalpy for the

42.3 Percent of Methane in Carbon Dioxide

Datum: Pure crystal of $CH_4 + CO_2$ at 0 K and zero pressure

$H_{P,T} - H_{o,o}$ (kJ mol^{-1})

P / T K bar	270	273.15	280	290	300	310	313.15	320
0	27.665	27.776	28.015	28.375	28.735	29.110	29.227	29.490
10.00	27.325	27.445	27.690	28.080	28.460	28.855	28.980	29.255
20.00	26.950	27.085	27.360	27.770	28.175	28.590	28.720	29.010
30.00	26.545	26.690	27.000	27.445	27.885	28.315	28.450	28.750
40.00	26.090	26.250	26.610	27.090	27.570	28.040	28.180	28.485
50.00	25.570	25.750	26.170	26.705	27.230	27.745	27.890	28.205
60.00	24.965	25.180	25.675	26.290	26.875	27.430	27.590	27.930
70.00	24.250	24.510	25.090	25.815	26.495	27.105	27.265	27.635
80.00	23.400	23.700	24.380	25.265	26.050	26.755	26.930	27.335
90.00	22.480	22.820	23.610	24.700	25.550	26.400	26.595	27.030
100.00	21.630	22.065	22.985	24.170	25.050	26.030	26.260	26.720
110.00	21.065	21.550	22.470	23.690	24.670	25.670	25.920	26.415
120.00	20.770	21.195	22.070	23.280	24.360	25.325	25.595	26.105
130.00	20.620	20.920	21.780	22.970	24.055	24.990	25.260	25.790
137.89	20.550	20.770	21.650	22.805	23.815	24.730	24.989	25.535

TABLE VIII(continued)

CH_4(42.3%) - CO_2

P / T K, bar	$H_{P,T} - H_{o,o}$ (kJ mol^{-1})						
	330	333.15	340	350	360	363.15	370
0	29.875	29.980	30.255	30.645	31.025	31.142	31.405
10.00	29.645	29.770	30.030	30.440	30.830	30.955	31.230
20.00	29.410	29.550	29.815	30.235	30.640	30.770	31.050
30.00	29.175	29.320	29.600	30.025	30.445	30.580	30.880
40.00	28.930	29.080	29.380	29.810	30.250	30.390	30.695
50.00	28.680	28.830	29.150	29.605	30.060	30.195	30.510
60.00	28.420	28.575	28.910	29.395	29.870	30.005	30.330
70.00	28.150	28.320	28.670	29.180	29.665	29.805	30.145
80.00	27.880	28.055	28.415	28.945	29.450	29.605	29.965
90.00	27.610	27.790	28.160	28.710	29.245	29.405	29.780
100.00	27.345	27.530	27.915	28.485	29.040	29.210	29.590
110.00	27.070	27.260	27.670	28.265	28.840	29.015	29.405
120.00	26.795	26.995	27.425	28.050	28.650	28.830	29.230
130.00	26.515	26.730	27.180	27.830	28.450	28.640	29.050
137.89	26.290	26.521	26.995	27.665	28.305	28.440	28.915

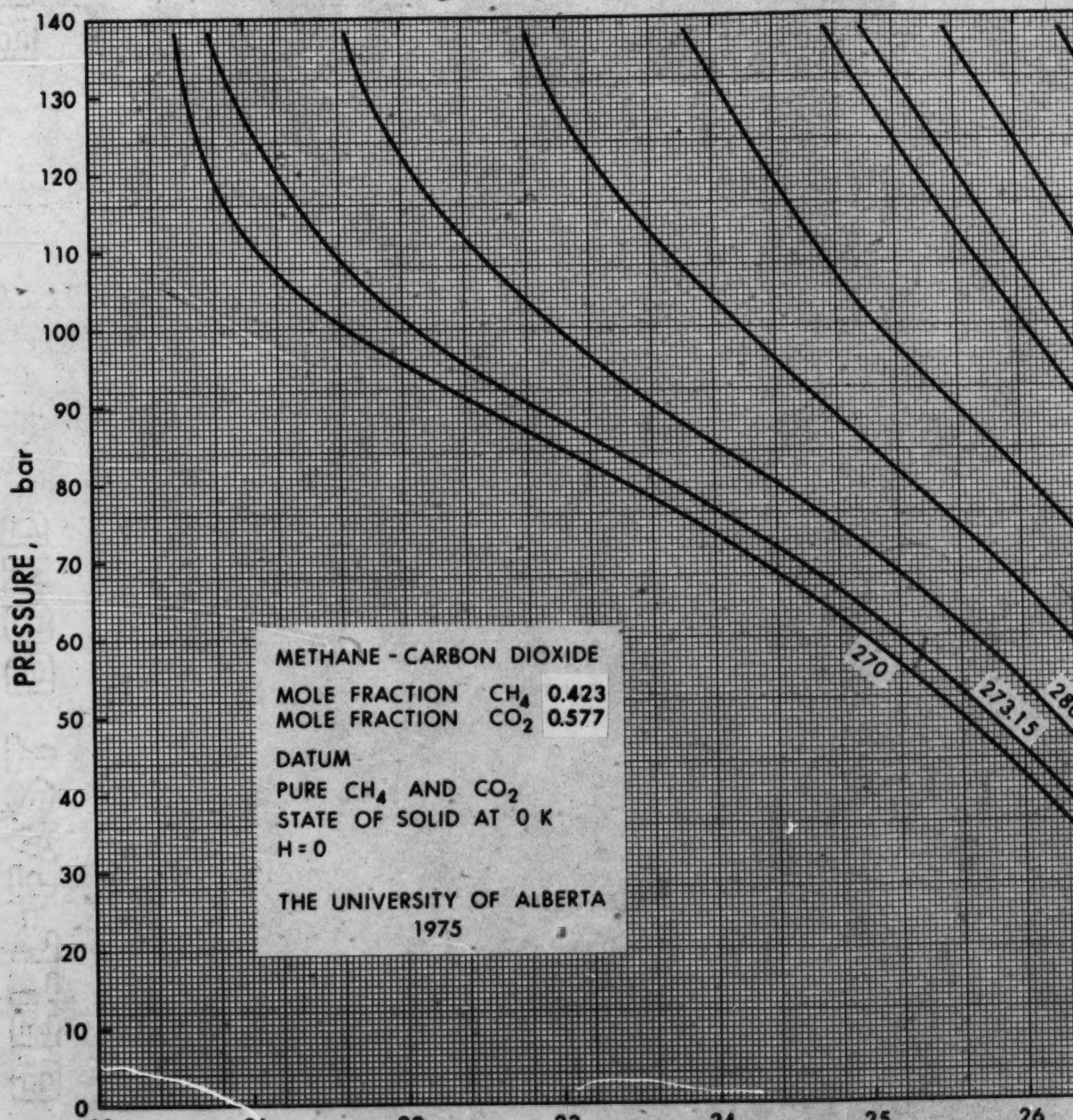
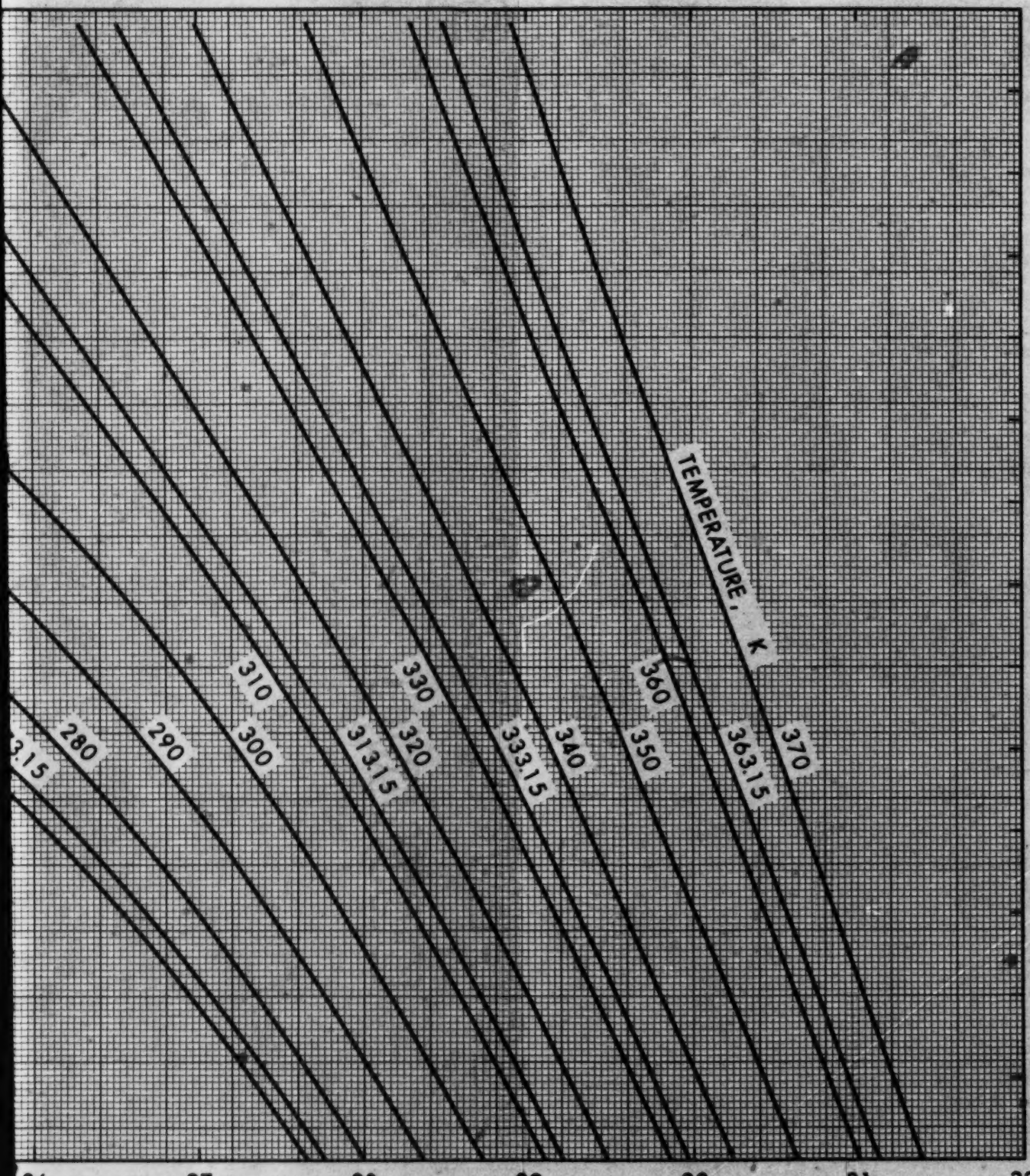


FIGURE 18. Pressure – Temperature – Enthalpy Diagram



iagram for 42.3 per cent of Methane in Carbon Dioxide

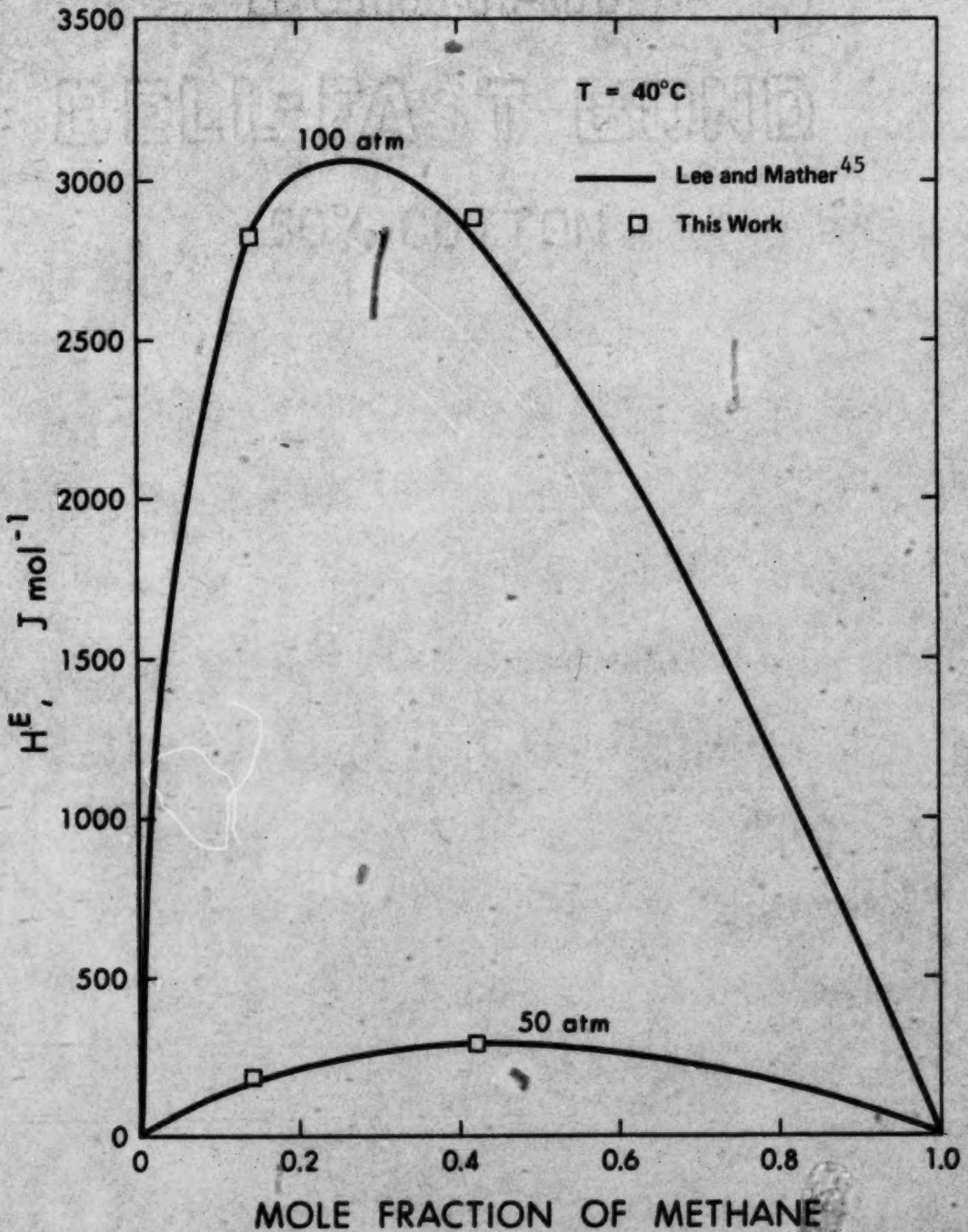


FIGURE 19. Comparison of Excess Enthalpy for Methane – Carbon Dioxide Mixtures

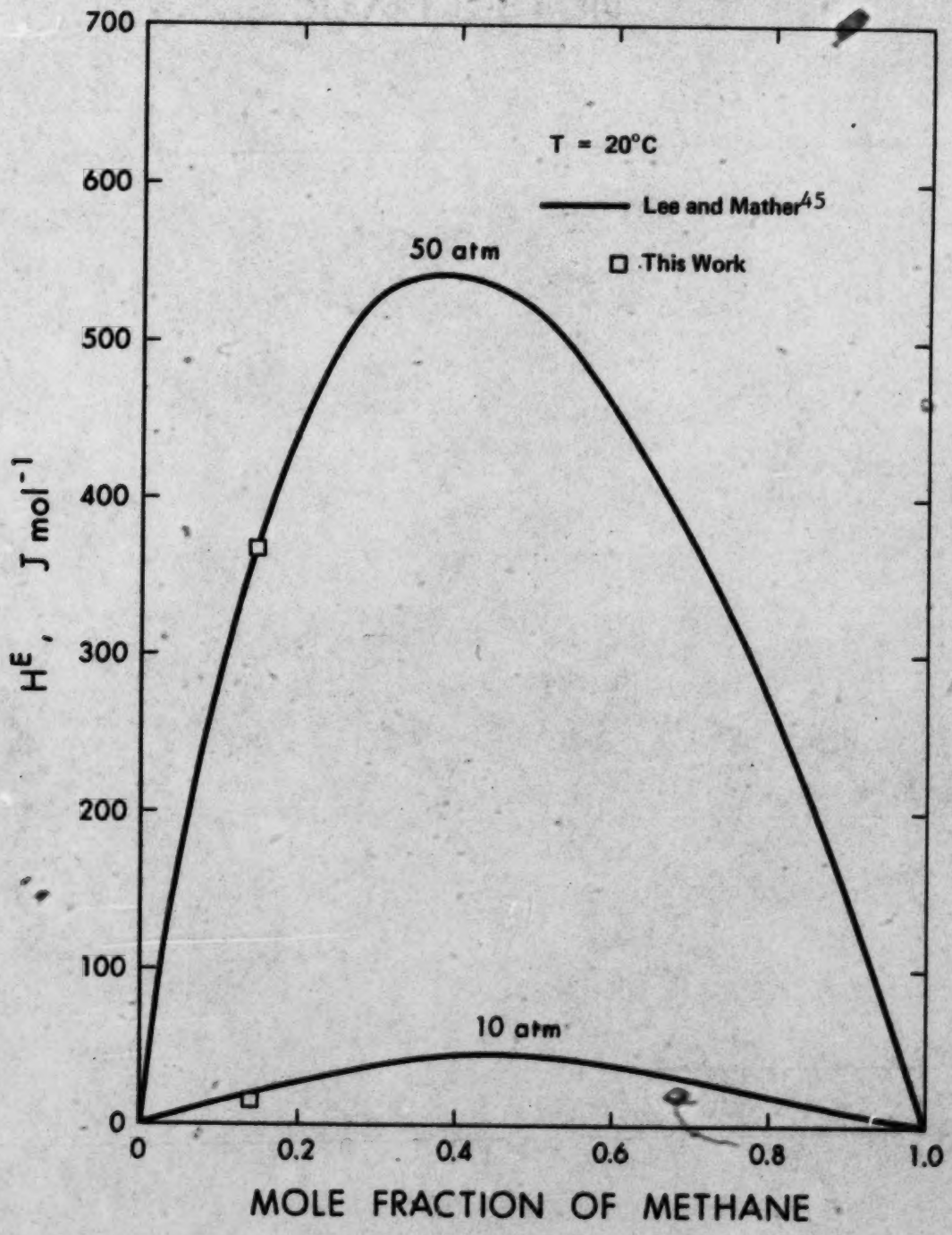


FIGURE 20. Comparison of Excess Enthalpy for Methane – Carbon Dioxide Mixture

Experimental Results With Equimolal Methane - Carbon Dioxide - Nitrogen Mixture

The measurements of the isothermal throttling coefficient were made on an equimolal mixture of methane, carbon dioxide and nitrogen. The pressure range of the measurements was from 300 to 2000 psia and the three temperatures were 10, -10 and -30°C. The composition of the mixture was determined by the gas chromatograph and is given in Table IX.

The smoothed isothermal data is tabulated at Table X and is shown in Figure 21. Values of ϕ at zero pressure were calculated from the virial coefficients given by Dymond and Smith[24] and Ng[63]. The calculation of ϕ° is shown in Appendix C.

TABLE IX

Composition of Equimolal Methane - Carbon Dioxide - Nitrogen Mixture

Composition	Mole Fraction
Methane	0.333
Nitrogen	0.333
Carbon dioxide	0.334

TABLE X

ISOTHERMAL THROTTLING COEFFICIENTS FOR THE EQUIMOLAL MIXTURE OF CO_2 - CH_4 - N_2

$-\phi$ (J mol^{-1} bar^{-1})

PRESSURE (bar)	Temperature, °C 10	-10	-30
0*	19.04	22.80	26.03
10	19.50	23.62	27.55
20	19.98	24.45	29.22
30	20.65	25.31	31.30
40	21.17	26.17	33.72
50	21.60	27.06	36.59
60	21.95	28.03	39.56
70	22.21	28.88	41.97
80	22.34	29.33	43.01
90	22.27	29.20	41.73
100	21.93	28.50	37.68
110	21.34	27.28	32.15
120	20.54	25.54	26.72
130	19.50	23.19	22.00
137	18.63	21.14	19.19

* $B - T\frac{dB}{dT}$

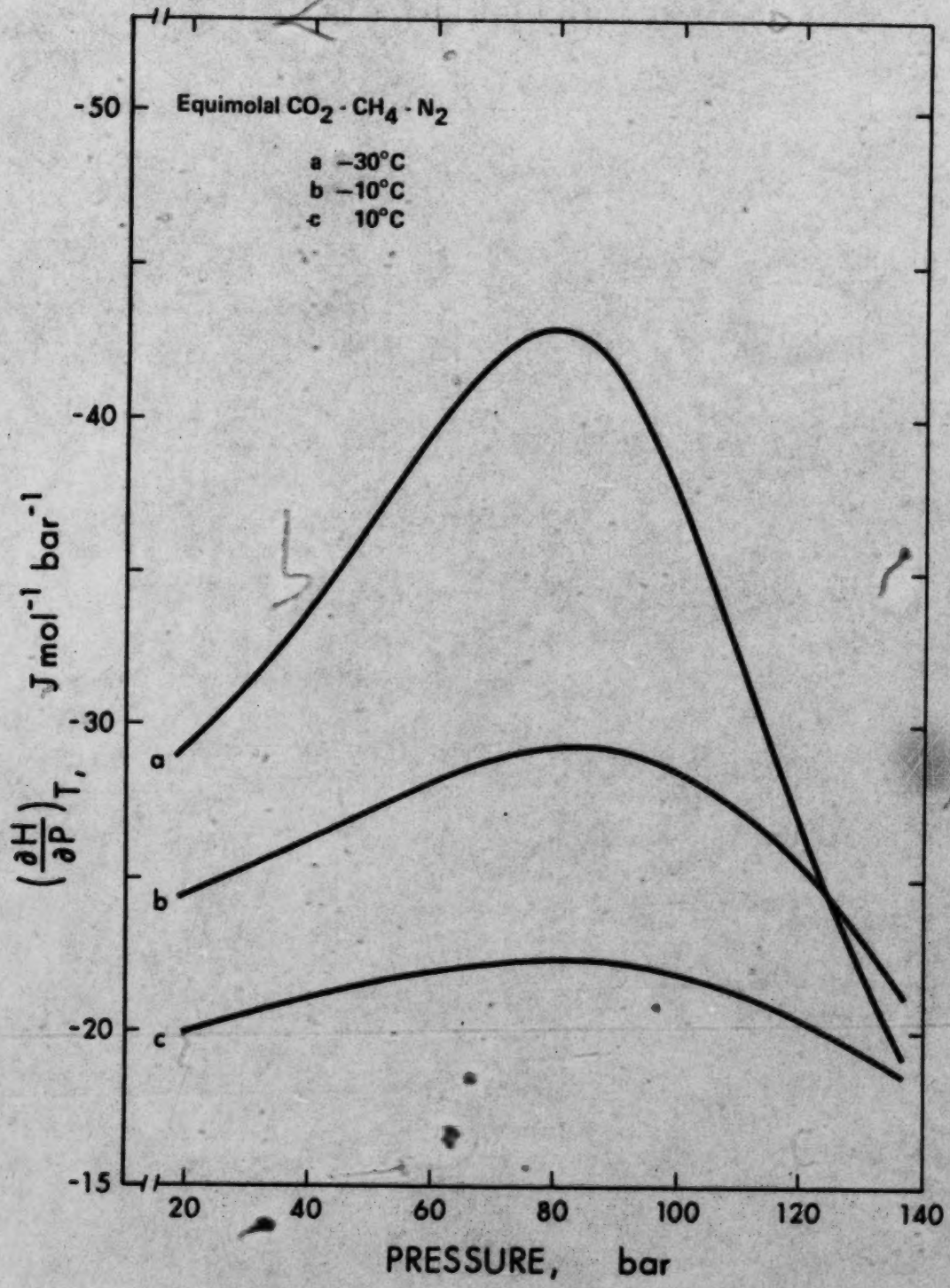


FIGURE 21. Isothermal Throttling Coefficient of the Equimolal Mixture of Methane, Carbon Dioxide and Nitrogen

Comparison of Experimental Results

Isothermal enthalpy departures for the mixture were calculated by integration of isothermal throttling coefficients with respect to pressure. The results were used to study the possibility of predicting ternary or multicomponent mixtures by using the binary experimental data. The experimental binary excess enthalpy data are from Lee and Mather[44,45] for carbon dioxide-methane system and nitrogen-carbon dioxide system. The experimental excess enthalpy data of nitrogen-methane system are from Klein et al.[40] Pure component enthalpy data of nitrogen and methane are from Din[23] and carbon dioxide is from Vukalovich and Altunin[85].

Due to the limitation of the experimental excess enthalpy data available, the comparison is made only on isotherm of 10°C. The enthalpy departure of each equimolal binary system at 10°C and several different pressures was calculated from data of experimental excess enthalpy of the binary system and enthalpy of the pure component by the following relation,

$$\Delta \underline{H}_{ij} = \underline{H}^{E}_{ij} + \frac{1}{2}(\underline{H}_i + \underline{H}_j) - \frac{1}{2}(\underline{H}^{\circ}_i + \underline{H}^{\circ}_j) \qquad (28)$$

where $\Delta \underline{H}_{ij}$ is molal enthalpy departure of equimolal mixture of i and j

$\underline{H}^{E}_{ij}$ is molal excess enthalpy of equimolal mixture of i and j

$\underline{H}_i, \underline{H}_j$ are molal enthalpy of i and j respectively

and $\underline{H}^{\circ}_i, \underline{H}^{\circ}_j$ are molal enthalpy at zero pressure of i and j respectively.

The molal enthalpy departure of the equimolal ternary mixture can be calculated as follows:

$$\Delta \underline{H}_{m,T,P} = \frac{1}{3}(\Delta \underline{H}_{12} + \Delta \underline{H}_{23} + \Delta \underline{H}_{13})_{T,P} \qquad (29)$$

The molal enthalpy departure of the equimolal ternary mixture of methane, carbon dioxide and nitrogen was also calculated by using BWR equation of

state with Bishnoi and Robinson mixing rules and parameters[11].

The comparison between experimental results of this work and values calculated from binary data is shown in Figure 22. The prediction by BWR equation of state is seen to be in excellent agreement with these experimental results. The lack of agreement between this experimental data and the values calculated from binary data may be due to not taking account of ternary interactions.

Experimental Results With Equimolal Methane - Carbon Dioxide - Ethane Mixture

Data of isothermal throttling coefficients were obtained at six isotherms for the equimolal mixture. The composition of the mixture which was determined by gas chromatograph is given in Table XI. The pressure range was from 250 to 2000 psia and the six isotherms are -10, 0, 20, 40, 60 and 90°C.

TABLE XI

Composition of Equimolal Methane - Carbon Dioxide - Ethane Mixture

Composition	Mole Fraction
Methane	0.340
Ethane	0.325
Carbon dioxide	0.335

The raw experimental data was treated by computer reduction method and the smooth isothermal throttling coefficients are tabulated in

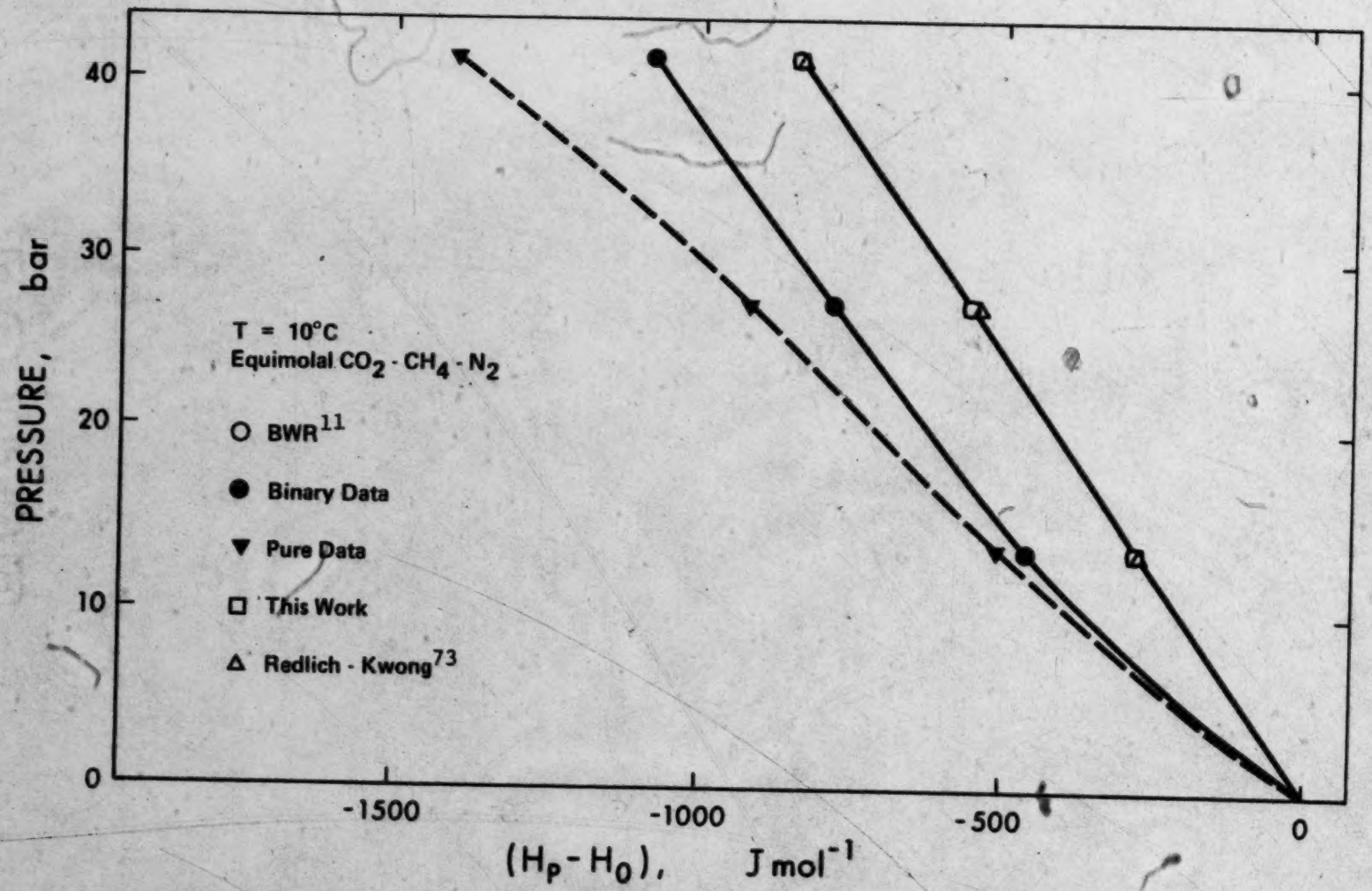


FIGURE 22. Enthalpy Departures for Equimolal Mixture of Methane, Carbon Dioxide and Nitrogen at 10°C

Table XII. The smooth isothermal throttling coefficient at constant temperature is plotted as function of pressure and it is shown in Figure 23. The zero pressure isothermal throttling coefficients were determined from second virial coefficient[20,24,27,31,63,101] by using Equation (14). The calculation of ϕ° is shown in Appendix C.

Comparison of Results

Peterson and Wilson reported isothermal enthalpy departure from 20 to 2000 psia for this mixture at temperature from -50°F to 300°F. Enthalpy departures were calculated from the experimental isothermal throttling data which are listed in Table XII by integration with respect to pressure. The values obtained were plotted as function of temperature at constant pressure. Figure 24 shows the comparison between experimental data of Peterson and Wilson[68] and this work. The agreement is seen to be very good.

Experimental Results with 50 Percent Methane in Carbon Dioxide and Ethane Mixture

Isothermal throttling coefficient determinations of this mixture were obtained in the gaseous region at temperatures from -10 to 90°C, at pressure from 250 to 2000 psia. The composition of this mixture was determined by gas chromatograph and the compositions are given in Table XIII.

TABLE XII

ISOTHERMAL THROTTLING COEFFICIENTS FOR THE

EQUIMOLAL CO_2 - CH_4 - C_2H_6 MIXTURE

$-\phi$ (J mol^{-1} bar^{-1})

PRESSURE (bar)	Temperature, °C					
	-10.0	0	20	40	60	90
0*	41.80	40.20	34.60	30.40	26.80	22.60
10	46.83	42.87	36.39	31.39	27.55	22.92
20	52.83	47.40	38.99	32.96	28.46	23.41
30	63.32	54.16	42.18	34.74	29.55	23.93
38	77.29	-	-	-	-	-
40	-	64.55	46.22	36.66	30.67	24.42
50	-	80.96	51.50	39.01	31.82	24.86
60	-	114.5	58.09	41.64	32.97	25.25
70	-	142.2	65.04	44.16	34.06	25.59
80	-	99.01	70.61	46.13	34.91	25.83
90	-	48.30	70.55	47.17	35.34	25.90
100	-	29.57	60.75	46.76	35.19	25.77
110	-	19.19	46.50	44.34	34.46	25.43
120	-	14.30	34.92	39.75	33.29	24.89
130	-	10.94	26.25	34.36	31.38	24.15
137	-	8.86	21.67	30.83	29.31	23.52

* $B - T\frac{dB}{dT}$

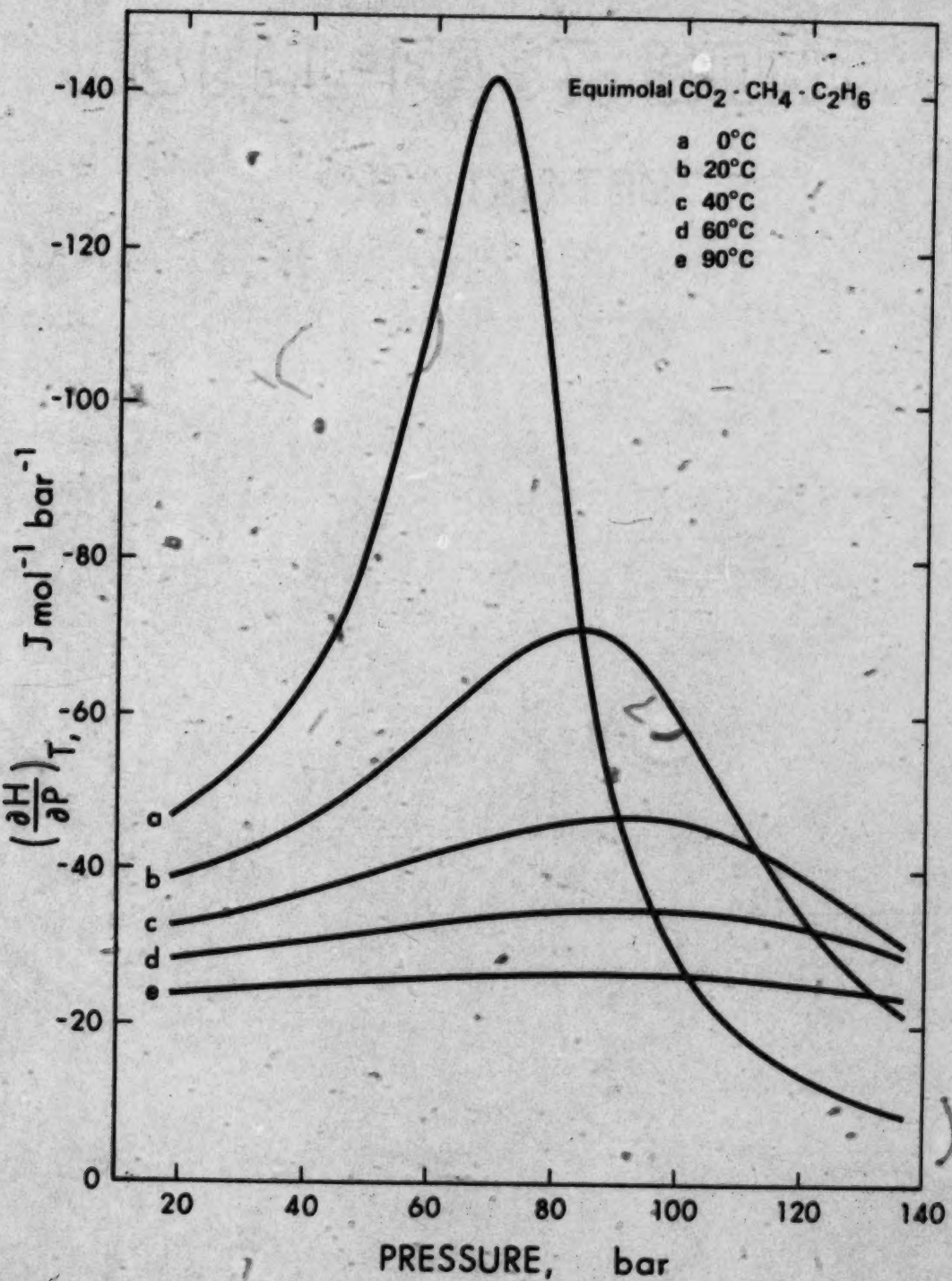


FIGURE 23. Isothermal Throttling Coefficient for the Equimolal Mixture of Methane, Carbon Dioxide and Ethane

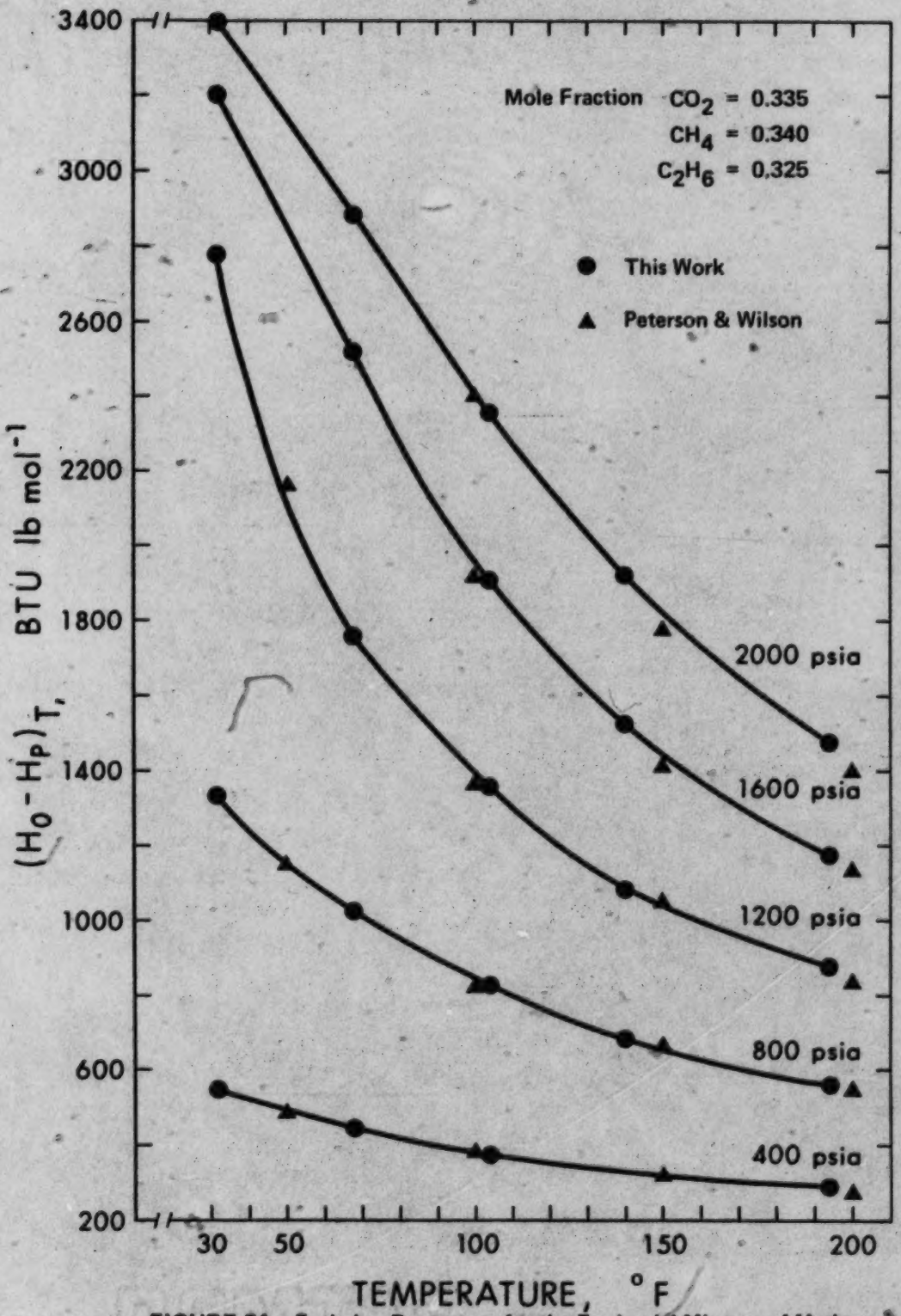


FIGURE 24. Enthalpy Departures for the Equimolal Mixture of Methane, Carbon Dioxide and Ethane

TABLE XIII

Composition of 50 Percent Methane in Carbon Dioxide and Ethane Mixture

Composition	Mole Fraction
Methane	0.514
Ethane	0.242
Carbon Dioxide	0.244

Isothermal throttling coefficients derived from the experimental data by computer reduction method are tabulated in Table XIV. A plot of the isothermal throttling coefficient at constant pressure as a function of temperature is shown in Figure 25.

Experimental Results with Equimolal Methane - Carbon Dioxide - Nitrogen - Ethane Mixture

Isothermal throttling coefficient determinations of this mixture were obtained in the gaseous region at temperatures from -30 to 60°C, at pressure from 250 to 2000 psia. The composition of this mixture was determined by the gas chromatograph and the compositions are given in Table XV.

TABLE XIV

ISOTHERMAL THROTTLING COEFFICIENTS FOR THE

50 PERCENT CH_4 IN CO_2 - C_2H_6 MIXTURE

$-\phi$ (J mol^{-1} bar^{-1})

PRESSURE (bar)	Temperature, °C					
	-10	0	20	40	60	90
0*	36.20	32.80	28.80	25.20	22.30	18.68
10	38.62	35.15	30.25	26.18	22.86	19.12
20	41.83	37.85	31.67	27.21	23.52	19.39
30	46.46	41.24	33.26	28.11	24.10	19.67
40	53.62	45.52	35.31	29.09	24.66	19.95
50	64.00	51.01	37.77	30.13	25.20	20.21
60	79.37	58.01	40.32	31.18	25.71	20.40
70	94.67	66.39	42.60	32.12	26.14	20.49
80	90.73	70.53	44.28	32.80	26.43	20.48
90	61.32	64.61	44.89	33.09	26.51	20.37
100	37.81	52.58	43.74	32.85	26.32	20.19
110	26.03	39.36	40.45	31.96	25.86	19.95
120	18.30	27.82	35.70	30.34	25.12	19.62
130	13.35	20.13	30.33	28.15	24.05	19.14
137	11.45	17.41	26.67	26.47	23.08	18.68

* $B - T\frac{dB}{dT}$

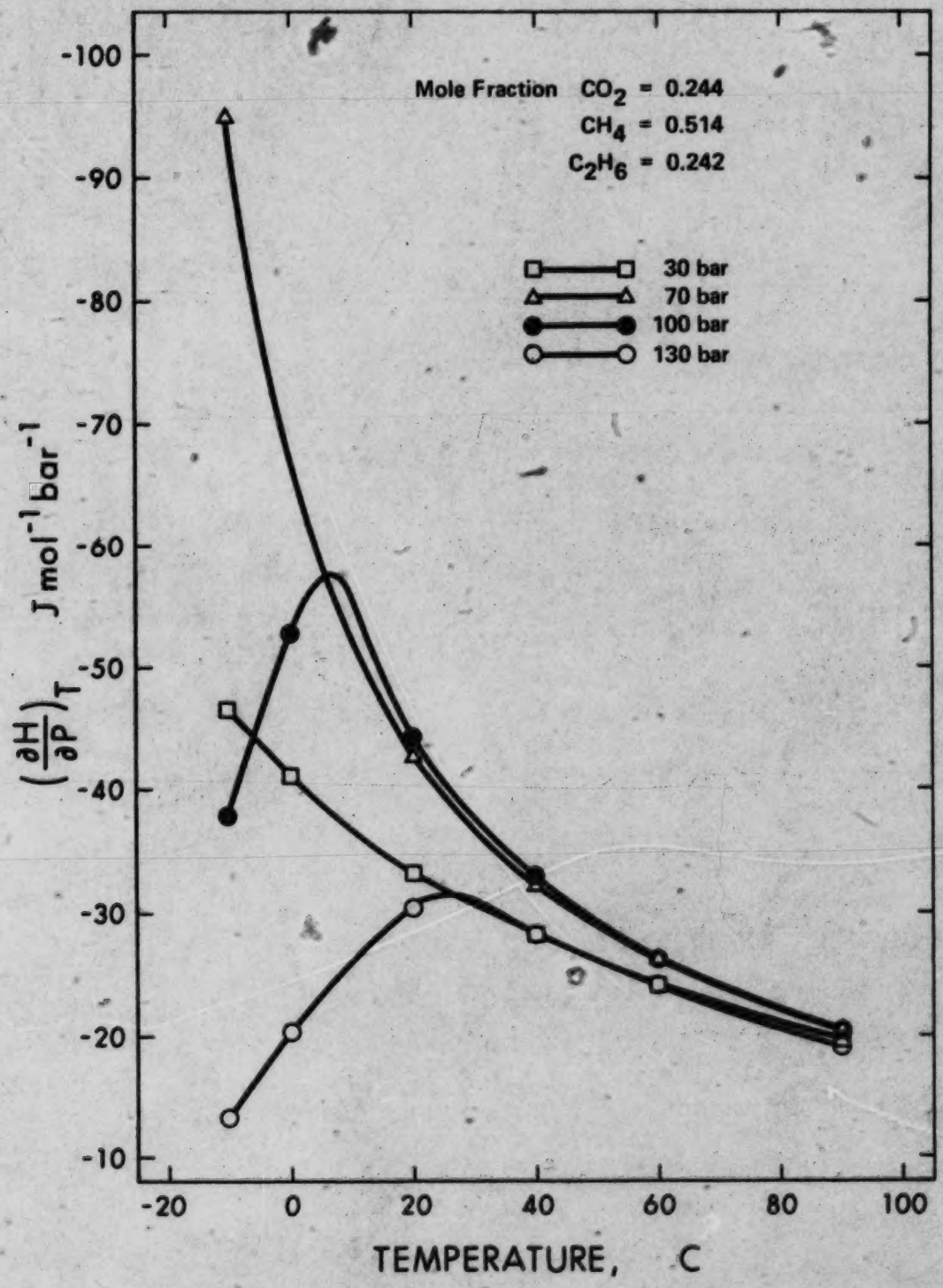


FIGURE 25. Isothermal Throttling Coefficient for the 50 Percent Mixture of Methane in Carbon Dioxide and Ethane

TABLE XV

Composition of Equimolal Methane - Carbon Dioxide - Nitrogen - Ethane Mixture

Composition	Mole Fraction
Methane	0.2535
Carbon Dioxide	0.2555
Ethane	0.2365
Nitrogen	0.2545

Smooth isothermal throttling coefficient of this mixture by this experiment are tabulated at Table XVI. A plot of the isothermal throttling coefficients at constant temperature as function of pressure is shown in Figure 26, Zero pressure isothermal throttling coefficients were calculated from second virial coefficients [20,24,27,31,64,70,101] by Equation (14) and the calculation of ϕ° is shown in Appendix C.

TABLE XVI

ISOTHERMAL THROTTLING COEFFICIENTS FOR THE EQUIMOLAL CO_2 - CH_4 - N_2 - C_2H_6 MIXTURE

$-\phi$ (J mol^{-1} bar^{-1})

PRESSURE (bar)	Temperature, °C				
	-30	-10	10	30	60
0*	35.90	31.40	27.20	23.60	19.50
10	38.00	32.50	27.96	24.08	19.62
20	43.52	34.40	28.92	24.78	19.87
27	47.50	-	-	-	-
30	-	37.47	30.29	25.47	20.12
40	-	41.35	31.81	26.26	20.43
50	-	45.46	33.38	26.93	20.70
60	-	49.27	34.90	27.47	20.84
70	-	52.03	36.13	27.91	20.88
80	-	52.72	36.73	28.07	20.80
90	-	50.28	36.41	28.07	20.60
93	35.77	-	-	-	-
100	27.77	43.96	35.08	27.51	20.28
110	19.47	35.30	32.75	26.54	19.85
120	14.34	26.88	29.50	25.25	19.29
130	11.05	21.19	25.86	23.69	18.54
137	9.39	19.42	23.55	22.13	17.88

* $B - T\frac{dB}{dT}$

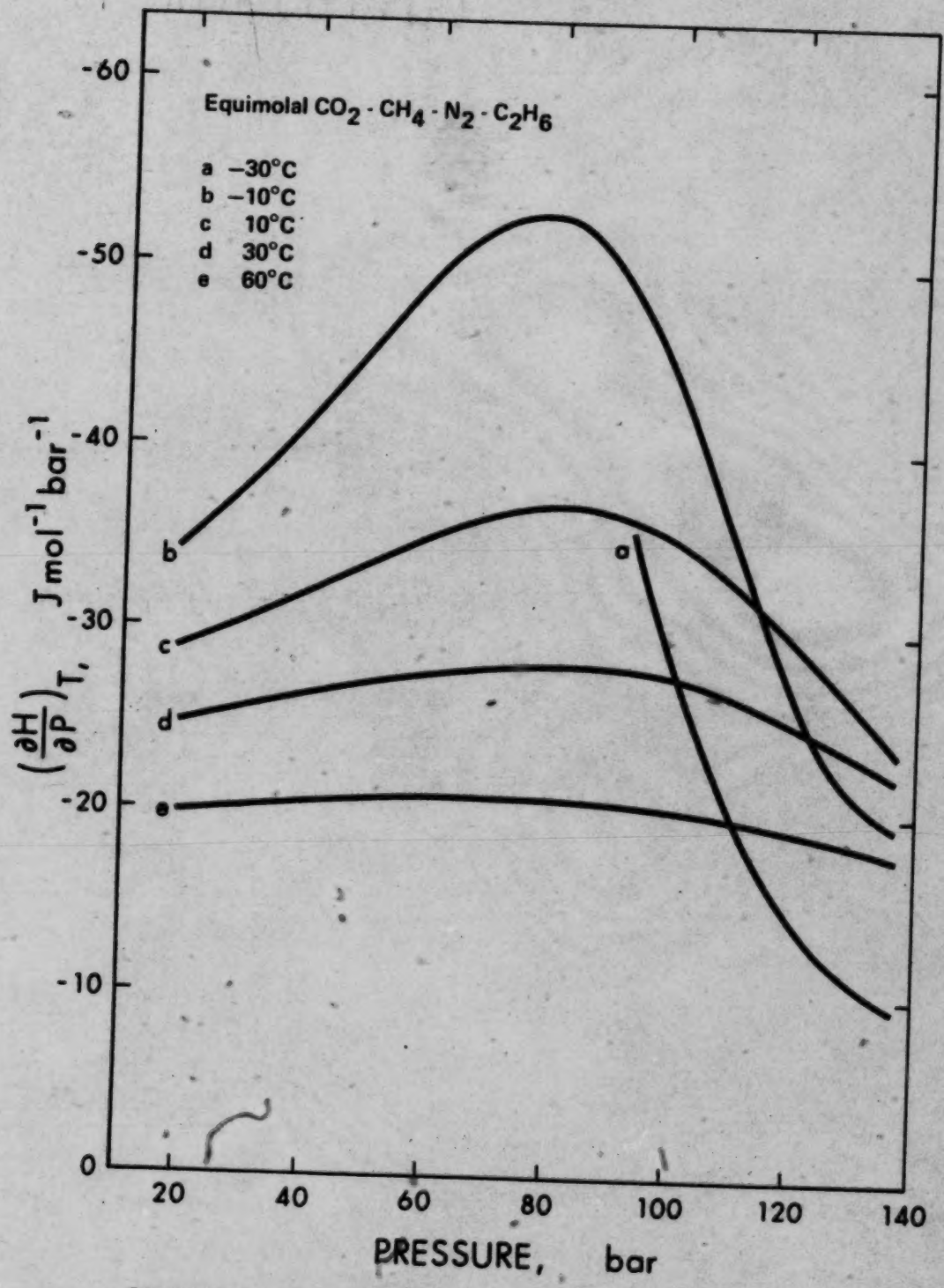


FIGURE 26. Isothermal Throttling Coefficient for the Equimolal Mixture of Methane, Carbon Dioxide, Nitrogen and Ethane

SECTION IV - EVALUATION AND EXTENSION OF METHODS OF PREDICTION

This section presents a review of the methods of prediction of thermodynamic properties and particularly enthalpy of mixtures. Two new methods are proposed for the enthalpy prediction.

To calculate the thermodynamic properties of a fluid or fluid mixture from a knowledge of molecular parameters by directly solving the equations of statistical mechanics, requires very detailed mathematical calculations as well as knowledge of the interactions between many particles. For this reason, no satisfactory solution has been achieved for all regions of enthalpy prediction. Statistical mechanics has been applied with some success in this endeavor especially with respect to the behavior of gases containing relatively simple molecules.

Although advances have been made in the area of predicting macroscopic properties, it appears that for some time to come less sophisticated methods of prediction must play an important role. To obtain quantitative representation of thermodynamic properties, assumptions are required which make use of experimental data and certain parameters or functional forms having no direct fundamental significance. These approaches and other methods developed from correlating thermodynamic data will be discussed.

Method of Prediction Based on Thermodynamic Data

A recent review of the available methods of prediction of enthalpies of fluid mixture at elevated pressure was made by Nathan[62], Mather[57] and Yesavage[97]. The main groups into which the methods can be divided are:

1. Estimation of partial enthalpies

2. Equivalent pure component method
3. Application of PVT data
4. Application of equations of state
5. Generalized corresponding states correlations

1. *Estimation of Partial Enthalpies*

The enthalpy per mole of a mixture, $\underline{H}_m$, can be determined exactly from a knowledge of the partial molal enthalpies of the individual components $\bar{H}_i$, by application of the expression

$$\underline{H}_m = \sum_i x_i \bar{H}_i \qquad (30)$$

The partial molal enthalpy of a component is generally a function of composition. For gases at zero pressure, the assumption that the enthalpy of a component in a mixture is the same as the enthalpy of the pure component is an accurate one. Therefore Equation (30) can be applied rigorously to establish the enthalpy of gaseous mixtures at zero pressure. In general, however, partial molal data are not abundant, and therefore, several methods of estimation have been suggested.

Very often the assumption is made that since hydrocarbons in a homologous series, are chemically similar, their solutions are ideal. Hence to compute a mixture properties, the sum of the property of each of the pure components (at the same temperature and total pressure) is taken in proportion to the quantity of the components present. This assumption may give good results at moderate pressures and relatively high temperatures. However, extreme care must be taken when applying this procedure since as Mather[57] has shown extreme values of the heat of mixing do exist, especially in critical regions. Charts for the pure

component enthalpies are given by Maxwell[60], Peters[67] and Scheibel and Jenny[75]. A difficulty arises in using these charts because it is not always possible to obtain the enthalpy data for the pure component for the conditions of temperature and pressure under which the mixture exists. Peters has derived auxiliary curves for estimation of partial enthalpies under those conditions and Maxwell used an extension of the vapor pressure curve for the partial enthalpy of a low-boiling component in a liquid mixture. In general, the plots presented by Peters were limited to a temperature range between -260 to +420°F at pressure up to 600 psia. Similarily, Maxwell's plots extend between -200 and +200°F at pressure below 150 atm.

A major drawback of this method is the fact that an enthalpy diagram must be available for every component present in a mixture.

2. *Equivalent Pure Component Method*

Several methods have been developed in which a new parameter is introduced to allow for the effect of composition. The data are usually presented as a series of enthalpy-temperature plots, there being a separate one for each pressure, with lines of this constant parameter. The forms that this parameter takes are most commonly the molal average boiling point, the average molecular weight or the mixture specific gravity.

Scheibel and Jenny[75] presented monographs based on the average molecular weight of a hydrocarbon mixture.

Papadopoulos et al.[65] showed that the molal average boiling point of a mixture defined as

$$M.A.B.P. = \sum_i x_i (B.P.)_i \qquad (31)$$

where the $(B.P.)_i$ are the pure component boiling points, for lighter hydrocarbons served to correlate values of a partial molal enthalpies calculated from an equation of state. At the same time Canjar and Edmister[13] employed the same correlation using the fugacity coefficients, employing a numerical technique for differentiation, and derived partial molal enthalpies for lighter hydrocarbons. Canjar and Peterka[14] prepared plots of the isothermal enthalpy departure as a function of temperature at pressure for mixtures with different molal average boiling points. The plots of Canjar and Peterka are restricted to the temperature range -200 to 500°F at pressures below 1500 psia for mixtures with molal average boiling points from -270 to 190°F.

3. *Application of P-V-T Data*

Accurate P-V-T data can be used to calculate the effect of pressure on enthalpy of fluids and fluid mixtures. If the volumetric data are available, the enthalpy can be calculated by use of the relation,

$$\underline{H}(T,P) = \underline{H}(T,0) + \int_0^P [\underline{V} - T(\frac{\partial \underline{V}}{\partial T})_P]dP_T \qquad (32)$$

where $\underline{H}(T,0)$, the enthalpy at zero pressure, can be determined for most simple fluids. This is evaluated from ideal gas enthalpies of pure fluids either from statistical mechanics or from measured data. The ideal mixture enthalpy is determined by applying Equation (30).

The term in brackets of Equation (32) under the integral sign involves the difference between two terms, one of which includes a derivative. As a result, extremely accurate volumetric data are required to yield reliable estimates of the effect of pressure on enthalpy. A reduction of accuracy of one order of magnitude is to be expected.

Volumetric data for mixtures of the required accuracy are available but very rare.

4. *Application of Equation of State*

A large number of equations of state have been proposed but only a few have been used for extensive calculations of enthalpies. In general, most equations of state serve to relate pressure P as the dependent variable to temperature, T, and specific volume $\underline{V}$ as independent variables. As a result, it is convenient to transform Equation (32) to,

$$\underline{H}(T,\infty) - \underline{H}(T,\underline{V}) = RT - P\underline{V} + \int_{\infty}^{\underline{V}} (P - T(\frac{\partial P}{\partial T})_{\underline{V}}]d\underline{V}_T \qquad (33)$$

The virial equation of state has a sound theoretical foundation and is free of arbitrary assumptions. The relations between virial coefficients and intermolecular potential functions can be derived from statistical mechanics and the composition dependence of the coefficients is known exactly. This equation is restricted to vapors since the power series relation tends to diverge at densities approaching those of liquids.

Relatively simple equations like the Redlich-Kwong[73] equation of state have been used for enthalpy predictions. Several modifications had been attempted to improve the prediction, such as those by Wilson[91], Soave[76] and Chaudron, Asselineau and Renon[17]. More complex equations such as the Benedict-Webb-Rubin[6] and Martin-Hou[56] have also been used to predict thermodynamic properties, including enthalpy. New mixing rules which were proposed by Bishnoi and Robinson[11] for the BWR parameters are claimed to improve the accuracy of such predictions. The modification of BWR equation by Starling[32,50,77,78] is claimed to improve the prediction especially at lower temperature regions. Other modifications of BWR type

of equations of state, such as that Bender[7] and McCarty[53] have also been proposed. Recently parameters for BWR[7,9,32,50,53,77] have been determined by multiproperties regressing on volumetric data, vapor pressure data, enthalpy and k-value data. This ensures thermodynamic consistency of all type of data.

Unfortunately neither accurate thermodynamic data nor parameters for equation of state such as BWR which need large amounts of experimental data are available for many components.

5. *Generalized Corresponding States Correlations*

Recently reviews of the application of the corresponding states principle have been presented by Stiel[81] and Leland and Chappelear[47]. These methods are based on the theory of corresponding states first put forward by van der Waals[62] in which he stated that all pure gases would have the same compressibility factor when measured at the same (reduced condition of) temperature and pressure. The law of corresponding states can be stated mathematically

$$\psi_i(T_{R_i}, P_{R_i}) = \psi_j(T_{R_j} = T_{R_i}, P_{R_j} = P_{R_i}) \qquad (34)$$

where the symbols ψ_i, and ψ_j represent corresponding dimensionless group properties of two fluids "i" and "j" given as function of their respective reduced temperature $T_{R_i} = T_i/T_{C_i}$ and reduced pressure $P_{R_i} = P_i/P_{C_i}$.

This statement of principle has become known as Two-Parameter Law of corresponding state because one must have knowledge of the two parameters (T_C and P_C) in order to apply it and must assume that there are only two adjustable parameters in the intermolecular potential in order to derive it from statistical mechanics.

Lydersen, Greenkorn and Hougen (LGH)[51] correlated the thermodynamic properties of pure compounds based on a modified corresponding states principle. This principle states that pure compound with the same critical compressibility Z_C values, the dimensionless groups of properties of two pure compounds have the same numerical values at corresponding reduced condition. The correlation of LGH has the form

$$\frac{\underline{H}(T,0) - \underline{H}(T,P)}{T_C} = \left[\frac{\underline{H}^0 - \underline{H}}{T_C}\right] + (Z_C - 0.27)[D] \qquad (35)$$

where the bracketed terms are presented as generalized functions in tabular form by the authors. The condition covered include $P_R \leq 30$ for $0.5 \leq T_R \leq 15$. Yen and Alexander[95] and Yen and Garcia-Rangel[96] improved the correlation of the isothermal effects on enthalpies for pure compounds with the aid of reliable literature data.

Pitzer et al.[19] employed the acentric factor ω, which is related to the shape of the reduced vapor pressure curve as the third parameter. The correlation of Curl and Pitzer[19] is given in the form,

$$\frac{\underline{H}(T,0) - \underline{H}(T,P)}{RT_C} = \left[\frac{\underline{H}^0 - \underline{H}}{RT_C}\right]^{(0)} + \omega\left[\frac{\underline{H}^0 - \underline{H}}{RT_C}\right]^{(1)} \qquad (36)$$

where the bracketed terms are somewhat different generalized function presented in tabular form by the authors. These tables cover the range of pressure for $P_R \leq 9$ for $0.8 \leq T_R \leq 4$. Revision of the original correlations which incorporated enthalpy data at elevated pressure in addition to PVT data have been presented recently (Yarborough[94]). Chao and Greenkorn[15] recently extended the Curl and Pitzer correlation tempera-

ture range down to $T_R = 0.35$. The extended enthalpy correlation was obtained upon differentiation of the generalized fugacity function previously developed by Chao et al.[16] and upon combining with calorimetric data in the literature.

Leach and Leland[42,43] extended the two parameter law of corresponding states to include fluids which have structural dissimilarity. Molecular shape factors were introduced which modified the critical temperature and critical volume of fluids whose molecular structures were dissimilar to those of a fluid for which thermodynamic data were available.

Molecular shape factors (θ_{ij} and ν_{ij}) of a fluid "i" relative to fluid "j" are defined mathematically by the equations

$$Z_i = Z_j \tag{37}$$

$$\left(\frac{\Delta H}{RT_C}\right)_i = \left(\frac{\Delta H}{RT_C}\right)_j \tag{38}$$

at corresponding modified reduced conditions,

$$\frac{T_i}{\theta_{ij} T_{C_i}} = \frac{T_j}{T_{C_j}} \tag{39}$$

$$\frac{V_i}{\nu_{ij} V_{C_i}} = \frac{V_j}{V_{C_j}} \tag{40}$$

where Z is the compressibility factor of the two fluids.

In general, the molecular shape factors of a fluid are functions of its temperature, density and intermolecular parameters. Leach[43] correlated the shape factor for isomeric and paraffin hydrocarbon using

methane as a reference. Watson and Rowlinson[90] and Gunning and Rowlinson[29] used the same correlation for non-hydrocarbon systems. The molecular shape factor can be extended to predict thermodynamic properties of the mixtures. The mixing rules have been suggested by Leach[43].

Application of Generalised Corresponding States Correlations to Mixtures

In applying the above correlation to mixtures, it is assumed that the reduced functions for a mixture behave in the same manner as those for a pure component. It is necessary to establish values of the three parameters for mixture. The concept of pseudocritical properties was first suggested by Kay[38]. The suggested linear form are:

$$T_{C_m} = \sum_i x_i T_{C_i} \tag{41}$$

$$P_{C_m} = \sum_i x_i P_{C_i} \tag{42}$$

and

$$\omega_m = \sum_i x_i \omega_i \tag{43}$$

There are several other mixing rules which have been proposed in the literature. The procedure and the original background of the derivation of the mixing rules is presented.

i) Method of Pitzer and Hultgren[69]

Pitzer and Hultgren had extended the three parameter acentric factor corresponding state theory to binary gas mixtures, using the pseudocritical concept. By studying the experimental volumetric data,

it was found that simple quadratic formulas could be used to represent the composition dependence of the three pseudoproperties of each mixture. Applied to the multicomponent mixture, the equations of the mixing rule are:

$$T_{C_m} = \sum_i \sum_j x_i x_j T_{C_{ij}} \tag{44}$$

$$P_{C_m} = \sum_i \sum_j x_i x_j P_{C_{ij}} \tag{45}$$

$$\omega_m = \sum_i \sum_j x_i x_j \omega_{ij} \tag{46}$$

The constants $T_{C_{ij}}$, $P_{C_{ij}}$ and ω_{ij} $(i \neq j)$, must be evaluated from data on binary mixtures. These mixing rules reduces to Kay's rules when the constants $T_{C_{ij}}$, $P_{C_{ij}}$ and ω_{ij} are taken as arithmetric average of the pure constants.

ii) Method of Joffe-Stewart, Burkhardt and Voo[34,35,82]

The equations of the mixing rules are given as,

$$T_{C_m} = \frac{K^2}{J} \tag{47}$$

$$P_{C_m} = \frac{T_{C_m}^2}{J} \tag{48}$$

$$K^2 = \frac{T_{C_m}^2}{P_{C_m}} = \left[\sum_i y_i \left(\frac{T_{C_i}}{P_{C_i}^{1/2}} \right) \right]^2 \tag{49}$$

$$J = \frac{T_{C_m}}{P_{C_m}} = \frac{1}{8} \sum_i \sum_j y_i y_j \left[\left(\frac{T_{C_i}}{P_{C_i}} \right)^{1/3} + \left(\frac{T_{C_j}}{P_{C_j}} \right)^{1/3} \right]^3 \tag{50}$$

These rules were originally suggested by the mixing rules for the constants

in van der Waals equation where,

$$a_m = \sum_i y_i a_i \tag{51}$$

$$b_m = \sum_i \sum_j y_i y_j b_{ij} \tag{52}$$

Since the van der Waals equation is a two parameter equation, the strict development is limited to mutually conformal substances. However, the rules can be applied to other mixtures by assuming a linear variation in the third parameter.

iii) *Method of Leland and Mueller*[46]

The problem of defining pseudocritical values for a multicomponent phase is analogous to the problem of writing the virial coefficients for the pure components. The second virial coefficient for an m-component mixture is related to the pure component virials by:

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \tag{53}$$

Leland and Mueller obtained the mixing rules by equating terms of a second virial coefficient expression for mixtures with those of a pure component and making appropriate simplifying assumptions. The pseudocritical constants are given as

$$T_{C_m} = \left[\frac{\sum_i \sum_j y_i y_j \left(\frac{Z_C T_C^{\alpha+1}}{P_C} \right)_i^{1/\alpha} \left(\frac{Z_C T_C^{\alpha+1}}{P_C} \right)_j^{1/\alpha}}{\sum_i \sum_j y_i y_j \left[\frac{1}{2} \left(\frac{Z_C T_C}{P_C} \right)_i^{1/3} + \frac{1}{2} \left(\frac{Z_C T_C}{P_C} \right)_j^{1/3} \right]^3} \right]^{1/\alpha} \tag{54}$$

$$P_{C_m} = \frac{T_{C_m} \sum_i y_i Z_{C_i}}{\sum_i \sum_j y_i y_j \left[\frac{1}{2} \left(\frac{Z_C T_C}{P_C} \right)_i^{1/3} + \frac{1}{2} \left(\frac{Z_C T_C}{P_C} \right)_j^{1/3} \right]^3} \qquad (55)$$

where α is a function of

$$\frac{T \sum_i y_i P_{C_i}}{P \sum_i y_i T_{C_i}}$$

and is tabulated by the authors. The pseudocritical constant obtained by this method is not only function of components of mixture but also function of temperature and pressure. Again the third parameter is assumed to be linear variation for the mixture.

iv) Method of Prausnitz and Gunn[71]

The mixing rules of Prausnitz and Gunn are also suggested from relations for the second virial coefficient of conformal substances. These rules are given as:

$$T_{C_m} = \frac{\beta + \sqrt{\beta^2 + r V_{C_m} \gamma}}{2 s V_{C_m}} \qquad (56)$$

$$V_{C_m} = \sum_i \sum_j y_i y_j V_{C_{ij}} \qquad (57)$$

$$P_{C_m} = \frac{R T_{C_m}}{V_{C_m}} \sum_i y_i Z_{C_i} \qquad (58)$$

$$\omega_m = \sum_i y_i \omega_i \tag{59}$$

where Z_{C_i} can be obtained from

$$Z_{C_i} = 0.291 - 0.08\ \omega_i \tag{60}$$

The quantities β and γ are computed,

$$\beta = \sum_i \sum_j y_i y_j\ (T_C V_C)_{ij} \tag{61}$$

$$\gamma = \sum_i \sum_j y_i y_j\ (V_C T_C^{\,2})_{ij} \tag{62}$$

where

$$T_{C_{ij}} = (T_{C_i} T_{C_j})^{1/2} - \Delta T_{C_{ij}} \tag{63}$$

$$V_{C_{ij}} = \tfrac{1}{2}(V_{C_i} + V_{C_j}) - \Delta V_{C_{ij}} \tag{64}$$

where the Δ terms are small correction terms depending on the nature of the binary pairs. The quantities r and s are functions of T_R and ω tabulated by the authors.

Prausnitz and Gunn also recommended the following simplified rules,

$$\omega_m = \sum_i y_i \omega_i \tag{59}$$

$$T_{C_m} = \sum_i y_i T_{C_i} \tag{41}$$

$$P_{C_m} = \frac{RT_{C_m}}{\sum_i y_i V_{C_i}} \sum_i y_i Z_{C_i} \qquad (65)$$

where again Z_{C_i} is given by Equation (60).

v) Method of Barner and Quinlan[5]

Barner and Quinlan suggested the mixing rules based on a modified form of Redlich-Kwong equation of state (Chueh and Prausnitz[18]). The mixing rules for the two constants of the equation of state is given by Joffe and Zudkevitch[36] as,

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \qquad (66)$$

$$b_m = \sum_i \sum_j y_i y_j b_{ij} \qquad (52)$$

The suggested pseudocritical constant of the mixture is given by

$$T_{C_m} = \sum_i \sum_j y_i y_j T_{C_{ij}} \qquad (44)$$

$$V_{C_m} = \sum_i \sum_j y_i y_j V_{C_{ij}} \qquad (67)$$

$$\omega_m = \sum_i y_i \omega_i \qquad (59)$$

$$Z_C = 0.291 - 0.08\,\omega \qquad (60)$$

$$P_{C_m} = \frac{RZ_{C_m} T_{C_m}}{V_{C_m}} \qquad (68)$$

where

$$T_{C_{ij}} = (T_{C_i} + T_{C_j})(K_{ij}/2) \tag{69}$$

$$V_{C_{ij}} = \frac{1}{8}\left[V_{C_i}^{1/3} + V_{C_j}^{1/3}\right]^3 \tag{70}$$

The interaction constants K_{ij} are tabulated by the authors. K_{ij} have been generalized as a function of V_{C_i}/V_{C_j} and are also given by the authors.

vi) *Modified Method of Gunn*

Gunn[28] developed a corresponding states theory for fluid mixture. The pseudocritical temperature is obtained by using generalized equation for second virial coefficient of Curl and Pitzer[70] and the mixing rule for second virial coefficient.

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \tag{53}$$

$$B_{R_m} = \frac{B_m}{V_{C_m}} = B_{R_m}^{(0)} + \omega_m B_{R_m}^{(1)} \tag{71}$$

The rigorous expression for the scaling temperature is obtained by equating Equation (53) and (71).

$$V_{C_m}\left[B_{R_m}^{(0)}\left(\frac{T}{T_{C_m}}\right) + \omega_m B_{R_m}^{(1)}\left(\frac{T}{T_{C_m}}\right)\right] = \sum_i \sum_j \left[B_{R_{ij}}^{(0)}\left(\frac{T}{T_{C_{ij}}}\right) + \omega_{ij} B_{R_{ij}}^{(1)}\left(\frac{T}{T_{C_{ij}}}\right)\right] V_{C_{ij}} \tag{72}$$

where

$$\omega_m = \left[\sum_i \sum_j y_i y_j V_{C_{ij}} \omega_{ij}\right] V_{C_m}^{-1} \tag{73}$$

$$V_{C_m} = \sum_i \sum_j y_i y_j V_{C_{ij}} \tag{67}$$

A new correlation of second virial coefficient of both polar and non-polar system presented by Tsonopoulos[84] replaced that of Curl and Pitzer[70]. The new correlation for non-polar system is given by,

$$\frac{BP_C}{RT_C} = f^{(0)}\left(\frac{T}{T_C}\right) + \omega f^{(1)}\left(\frac{T}{T_C}\right) \tag{74}$$

where

$$f^{(0)}\left(\frac{T}{T_C}\right) = 0.1445 - \frac{0.330}{T_R} - \frac{0.1385}{T_R^2} - \frac{0.0121}{T_R^3} - \frac{0.000607}{T_R^8} \tag{75}$$

$$f^{(1)}\left(\frac{T}{T_C}\right) = 0.0637 + \frac{0.331}{T_R^2} - \frac{0.423}{T_R^3} - \frac{0.008}{T_R^8} \tag{76}$$

Replace Equation (71) by (74),

$$B_m = \left(\frac{RT_{C_m}}{P_{C_m}}\right)\left[f^{(0)}\left(\frac{T}{T_{C_m}}\right) + \omega_m f^{(1)}\left(\frac{T}{T_{C_{ij}}}\right)\right]$$

$$= \sum_i \sum_j y_i y_j \left[\frac{RT_{C_{ij}}}{P_{C_{ij}}}\right]\left[f^{(0)}\left(\frac{T}{T_{C_{ij}}}\right) + \omega_{ij} f^{(1)}\left(\frac{T}{T_{C_{ij}}}\right)\right] \tag{77}$$

where

$$\omega_{ij} = \frac{1}{2}(\omega_i + \omega_j) \tag{78}$$

$$V_{C_{ij}} = \frac{1}{8}\left(V_{C_i}^{1/3} + V_{C_j}^{1/3}\right)^3 \tag{70}$$

$$T_{C_{ij}} = (T_{C_i} T_{C_j})^{1/2}(1 - k_{ij}) \tag{79}$$

$$P_{C_{ij}} = \frac{T_{C_{ij}} \left[\left(\frac{P_C V_C}{T_C} \right)_i + \left(\frac{P_C V_C}{T_C} \right)_i \right]}{2 V_{C_{ij}}} \tag{80}$$

$$V_{C_m} = \sum_i \sum_j y_i y_j V_{C_{ij}} \tag{67}$$

$$Z_{C_m} = 0.291 - 0.08\, \omega_m \tag{60}$$

$$\omega_m = \left[\sum_i \sum_j y_i y_j V_{C_{ij}} \omega_{ij} \right] / V_{C_m} \tag{73}$$

$$P_{C_m} = Z_{C_m} R T_{C_m} / V_{C_m} \tag{68}$$

The interaction constant k_{ij} is given by Prausnitz[72] or by fitting the experimental B_{ij} with Equation (74). The pseudocritical constant T_{C_m} and P_{C_m} is obtained by solving Equation (77) and (68) simultaneously.

vii) *Proposed Method (Soave-Redlich-Kwong Equation of State)*

A modified Redlich-Kwong equation of state has been proposed by Soave[76]. The parameter a in the original equation is suggested to be temperature dependent. The modified equation is,

$$P = \frac{RT}{\underline{V} - b} - \frac{a(T)}{\underline{V}(\underline{V} + b)} \tag{81}$$

where

$$a_i(T) = a_{C_i} \alpha_i(T) \tag{82}$$

$$a_{C_i} = 0.42747 \frac{R^2 T_{C_i}^2}{P_{C_i}} \tag{83}$$

$$b_i = 0.08664 \frac{RT_{C_i}}{P_{C_i}} \tag{84}$$

$$\alpha_i^{0.5}(T) = 1 + m_i[1 - (\frac{T}{T_{C_i}})^{0.5}] \tag{85}$$

$$m_i = 0.480 + 1.574\ \omega_i - 0.176\ \omega_i^2 \tag{86}$$

Applying the equation of state to the mixture, the mixing rules for the two parameters are,

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \tag{66}$$

$$b_m = \sum_i y_i b_i \tag{87}$$

$$a_{ij} = (1 - k_{ij})(a_i a_j)^{1/2} \tag{88}$$

where k_{ij} is an empirical correlation factor to be determined from the experimental vapor-liquid equilibrium data, for each binary component present in the mixture. Generalization of k_{ij} has been attempted[66].

Starting by substituting Equation (82), (84) and (88) into Equation (66) and (87) respectively,

$$\alpha_m(\frac{T}{T_{C_m}})\frac{T_{C_m}^2}{P_{C_m}} = \sum_i \sum_j y_i y_j \left[\frac{\alpha^{1/2}(\frac{T}{T_{C_i}})\alpha^{1/2}(\frac{T}{T_{C_j}})T_{C_i}T_{C_j}(1-k_{ij})}{P_{C_i}^{1/2}P_{C_j}^{1/2}}\right] \tag{89}$$

$$\frac{T_{C_m}}{P_{C_m}} = \sum_i y_i \frac{T_{C_i}}{P_{C_i}} \tag{90}$$

From Equation (90) to Equation (89),

$$\alpha_m T_{C_m} = \frac{\sum_i \sum_j y_i y_j \left[\frac{\alpha_i^{1/2} \alpha_j^{1/2} T_{C_i} T_{C_j} (1-k_{ij})}{P_{C_i}^{1/2} P_{C_j}^{1/2}} \right]}{\sum_i y_i \frac{T_{C_i}}{P_{C_i}}} \tag{91}$$

$$P_{C_m} = \frac{T_{C_m}}{\sum_i y_i \frac{T_{C_i}}{P_{C_i}}} \tag{92}$$

T_{C_m} and P_{C_m} are obtained by solving Equation (91) and (92) simultaneously. Here the linear variation for ω_m is assumed.

Evaluation of Nine Enthalpy Correlations

The nine correlations evaluated and compared in this study are shown in Table XVII. Six of the correlations used corresponding states method of Curl and Pitzer[19] with six different mixing rules and three of the correlations used equations of state. The following six mixing rules for mixtures which have been discussed above to estimate the pseudo-critical parameters for the Curl and Pitzer generalized correlation are: 1) method of Barner and Quinlan, 2) proposed method (Soave-Redlich-Kwong equation of state), 3) modified method of Gunn, 4) method of Prausnitz and Gunn, 5) method of Joffe-Stewart, Burkhardt and Voo, and 6) method of Leland and Mueller. The equation of state correlations are Starling-BWR[32,77], Soave-Redlich-Kwong[76] equation and Mark V[92] correlation.

In this study, the Curl and Pitzer[19] generalized correlation tables for enthalpy departure and the extended correlation temperature range of Chao and Greenkorn[15] were used. The linear interpolation, performed by computer was utilized in the calculation of the enthalpy departure.

Presented in Table XVIII are the data sources, number of data point, and temperature and pressure regions of the data for the sixteen fluid compositions studied in this evaluation.

Presented in Table XIX for each correlation are the average absolute deviations between predicted enthalpy departures and experimental enthalpy departures for each of the sixteen fluid compositions used in this study. The overall average absolute deviation for the total data points is given for each correlation in Table XIX. It is to be noted that the BWRS yields the lowest average absolute deviations. Results

TABLE XVII

CORRELATIONS EVALUATED IN THIS STUDY

Correlation	Abbreviation	Developers	References
Starling-BWR	BWRS	Starling	32, 77, 79
Soave-Redlich-Kwong	SRK	Soave	76
Mark V	Mark V	Wilson	92
Corresponding State +		Curl, Pitzer	19
Method of Barner & Quinlan	CPBQ	Barner, Quinlan	5
Proposed Method	CPNM	This work	-
Method of Prausnitz & Gunn	CPPG	Prausnitz, Gunn	71
Method of Joff-Stewart, Burkhardt & Voo	CPSV	Joffe,Stewart, Burkhardt, Voo	34, 35, 82
Method of Leland & Mueller	CPLM	Leland, Mueller	46
Modified Method of Gunn	CPMG	Gunn	28

TABLE XVIII

DATA SOURCE OF SYSTEMS STUDIED

System	References	No Data Points	Lowest T °F	Highest T °F	Highest P psia
42.3% N_2-56.6 CH_4	54,57	54	-250	250	2000
100% CH_4	37,97	35	-250	50	2000
94.8% CH_4-5.2% C_3H_8	55,57	47	-250	250	2000
88.3% CH_4-11.7% C_3H_8	57	47	-250	250	2000
72% CH_4-28% C_3H_8	57	45	-250	250	2000
49.4% CH_4-50.6% C_3H_8	97	45	-250	250	2000
23.4% CH_4-76.6% C_3H_8	97	50	-250	250	2000
36.6% CH_4-31.1% C_2H_6-32.3% C_3H_8	26	31	-240	240	2000
38.5% C_5H_{12}-61.5% C_6H_{12}	48	36	540	600	1400
59.7% C_5H_{12}-40.3% C_8H_{18}	49	66	75	600	1400
42.3% CH_4-57.7% CO_2	This work	20	32	194	2000
14.5% CH_4-85.5% CO_2	This work	22	50	194	2000
Equimolal CH_4-CO_2-N_2	This work	15	-22	50	2000
Equimolal CH_4-CO_2-C_2H_6	This work	25	32	194	2000
$CH_4(\frac{1}{2})$-$CO_2(\frac{1}{4})$-$C_2H_6(\frac{1}{4})$	This work	30	14	194	2000
Equimolal CH_4-CO_2-C_2H_6-N_2	This work	20	14	140	2000

TABLE XIX SUMMARY OF RESULTS OF ENTHALPY CORRELATION EVALUATION

Average $|\Delta| = (\Delta H_{exp} - \Delta H_{cal})$, Btu lb^{-1}

System \ Rules	BWRS	CPBQ	CPNM	CPPG	CPSV	CPLM	CPMG	SRK	Mark V
Methane	0.6*	1.6	1.6	1.6	1.6	1.6	1.6	2.5	3.2
C_1 (0.95) C_3 (0.05)	0.7*	1.7	1.6	2.2	1.7	2.0	6.4	2.2	2.3
C_1 (0.883) C_3 (0.117)	0.7*	1.9	1.7	2.4	2.5	2.1	**	1.4	1.7
C_1 (0.72) C_3 (0.28)	0.9*	2.4	2.0	2.6	4.1	2.8	**	1.2	1.6
C_1 (0.494) C_3 (0.506)	1.3*	3.2	3.0	3.9	5.6	2.5	**	1.0	1.4
C_1 (0.234) C_3 (0.766)	0.9*	1.6	1.7	4.4	3.2	1.6	**	1.1	1.5
CO_2 (0.577) CH_4 (0.423)	0.4	1.8	1.1	0.6	0.7	1.8	1.1	0.8	1.4
CO_2 (0.855) CH_4 (0.145)	0.8	1.9	1.3	1.1	1.1	1.3	1.1	1.0	1.2
CO_2(1/3) - N_2(1/3) - CH_4(1/3)	0.2	3.0	1.7	1.4	2.6	1.6	0.7	0.5	0.5
CO_2(1/3)-CH_4(1/3)-C_2H_6(1/3)	0.7	1.5	0.9	1.1	3.3	5.5	0.9	0.8	1.9

TABLE XIX SUMMARY OF RESULTS OF ENTHALPY CORRELATION EVALUATION

Average $|\Delta| = (\Delta H_{exp} - \Delta H_{cal})$, Btu lb^{-1}

(continued)

System \ Rules	BWRS	CPBQ	CPNM	CPPG	CPSV	CPLM	CPMG	SRK	Mark V
CO_2(1/4)-CH_4(1/2)-C_2H_6(1/3)	0.4	2.1	1.4	0.7	1.4	3.5	0.7	0.8	1.5
CO_2(1/4)-CH_4(1/4)-N_2(1/4)-C_2H_6(1/4)	0.7	1.3	0.9	0.7	0.9	4.0	0.7	0.4	0.4
CH_4 (0.566) -N_2 (0.434)	0.5*	0.9	1.0	1.3	1.1	1.6	**	0.8	1.0
CH_4-C_2H_6-C_3H_8 0.366-0.311-0.323	4.0*	3.9	3.9	2.9	2.1	6.3	**	0.9	1.3
n-C_5 (0.385) ECH_{12} (0.615)	1.8*	0.9	1.2	1.4	0.9	1.0	**	1.3	***
n-C_5-n-C_8 (0.597-0.403)	2.8*	2.4	2.4	2.3	4.3	2.4	**	4.0	3.0
Overall Average	0.9	2.0	1.70	1.91	2.32	2.6		1.21	1.60

* From Starling et al.[79]

** Poor prediction for liquid region

*** Not available for cyclohexane

obtained using method two listed above, gives the lowest average absolute deviations among the six methods.

The pseudocritical parameters (temperature and pressure) which were obtained by the five different methods for the mixtures of 49.4 mole percent methane in propane plot as function of temperature are shown in Figure 27 and 28. Pseudocritical temperature and pressure obtained by modified method of Gunn shows very large deviation from others. Pseudocritical temperature and pressure obtained by method of Leland and Mueller are the function of temperature and pressure. They can not be shown in Figure 27 and 28.

Conclusions

The conclusion of this study is the finding that the equations of state BWRS, Soave-RK, Mark V and the corresponding states with the proposed mixing rule which is derived from Soave-RK, are the most accurate of the nine enthalpy correlations tested. Conclusions relating to each correlation individually are given below.

Starling-BWR

The average absolute deviation for this correlation is 0.9 Btu/lb. This method is not a generalized correlation and therefore can be applied only when the parameters of this equation of state have been determined for each component in a mixture. Also binary data are needed to determine interaction constants.

Soave-Redlich-Kwong Equation of State

The average absolute deviation for this correlation is 1.21

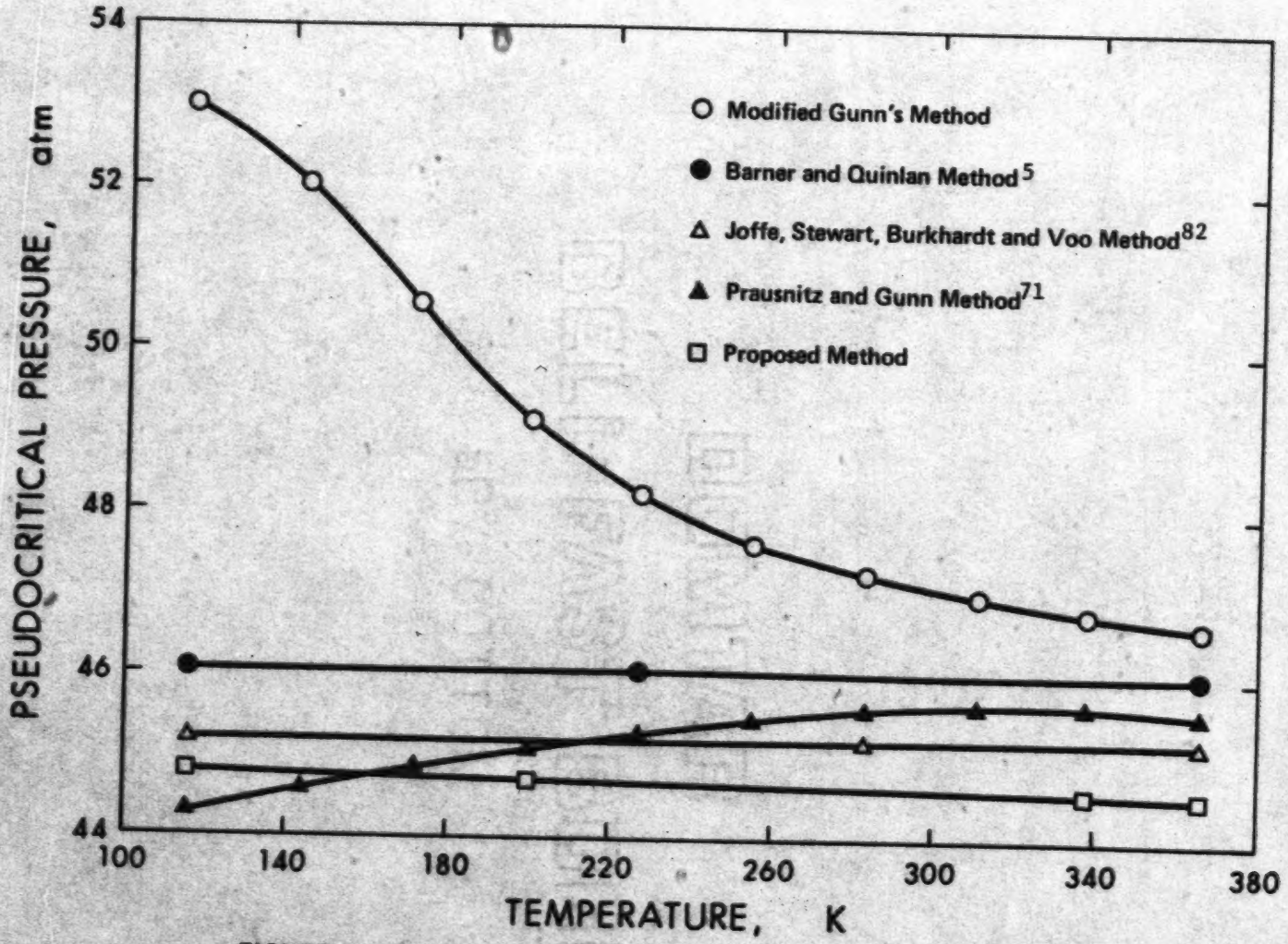


FIGURE 27. Pseudocritical Pressure at 49.4 percent Mixture of Methane in Propane

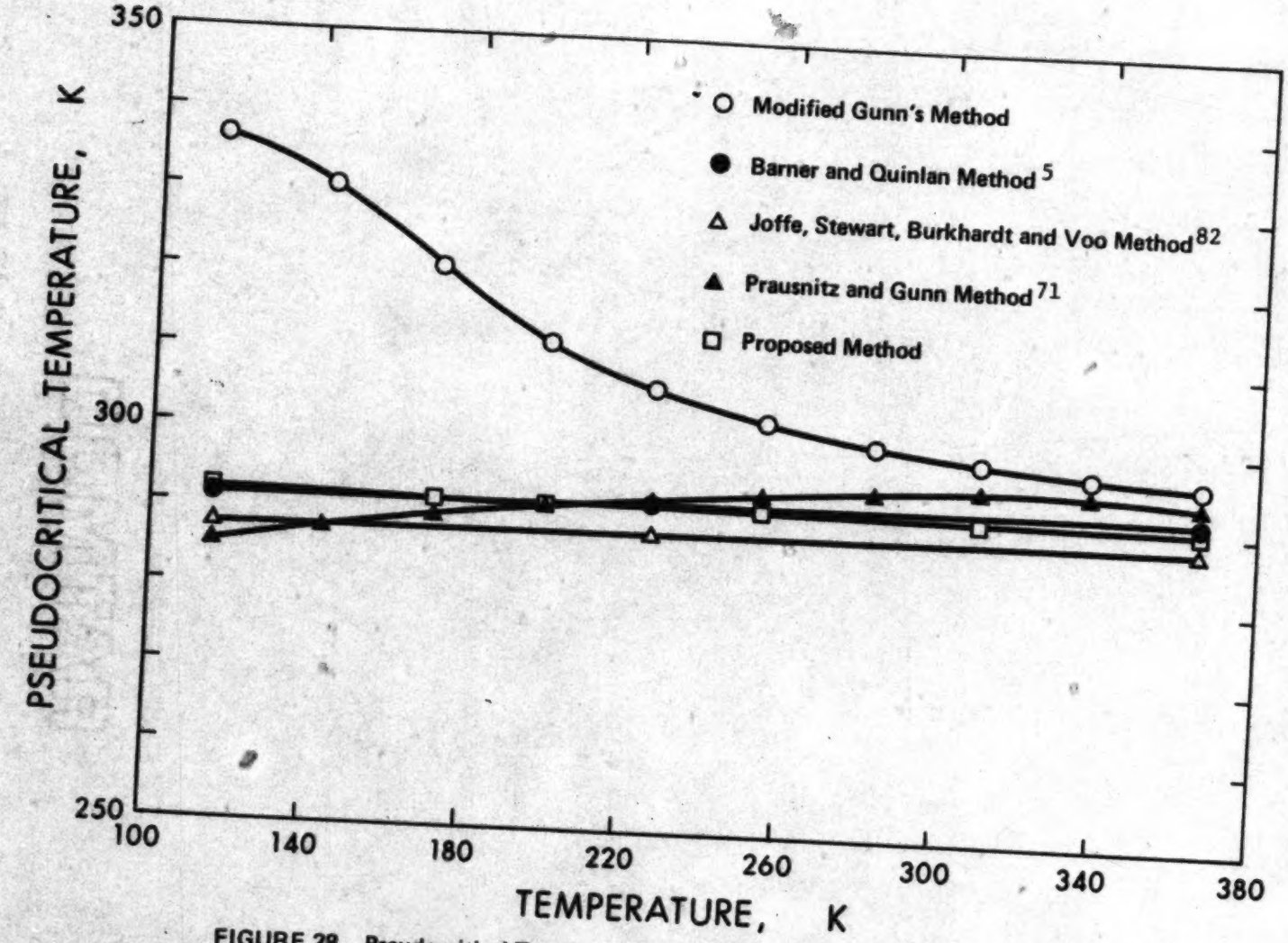


FIGURE 28. Pseudocritical Temperature of 49.4 percent Mixture of Methane in Propane

Btu/lb. This method can be considered as a generalized correlation because only critical properties and acentric factor of each component in mixture are required for the prediction. The only additional information is the interaction constant k_{ij} which has to be determined from the binary vapor-liquid equilibrium data. Generalization of k_{ij} for some system has been attempted[66]. This method requires very little computation time.

Mark V Computer Program

The average absolute deviation for this correlation is 1.60 Btu/lb. This correlation always predicts too high at low pressure and predicts too low at high pressure.

Corresponding State of Curl and Pitzer With Different Mixing Rules Proposed Method

The average absolute deviation for this correlation is 1.70 Btu/lb. The interaction constant k_{ij} for the Soave-Redlich-Kwong equation of state has to be determined from the binary vapor-liquid equilibrium data. The generalization of k_{ij} has been attempted.

Method of Barner and Quinlan

The average absolute deviation for this correlation is 2.0 Btu/lb. The mixing rules is derived from modified Redlich-Kwong equation of state (Chueh and Prausnitz[18]). Barner and Quinlan had generalized the binary interaction constant K_{ij} for most of the system. The pseudocritical temperature and pressure of the mixture are independent of the temperature of the system.

Method of Joffe, Stewart, Burkhardt and Voo

This correlation gives average absolute deviation of 2.32 Btu/lb. The mixing rules are derived based on van der Waals equation of state. No binary interaction constant is needed. It is not surprising that the prediction is less accurate than other methods which have one more adjustable parameter.

Method of Leland and Mueller

The average absolute deviation for this correlation is 2.6 Btu/lb. The pseudocritical temperature and pressure obtained by this method are both functions of the temperature and pressure of the system. This correlation gives very good prediction for some systems but gives very poor prediction for some other systems.

Modified Method of Gunn

This correlation gives very poor prediction in liquid region, but gives good prediction in gas region. The experimental data of this work are in gas region. It is shown in Table XIX that this correlation gives the lowest average absolute deviation among the corresponding states methods.

Method of Prausnitz and Gunn

The average absolute deviation for this correlation is 1.91 Btu/lb. Equation of the form $B_m = \Sigma \Sigma x_i x_j B_{ij}$ forms the theoretical

basis on which the prediction of pseudocritical constants is based. The two empirical constants $\Delta T_{C_{ij}}$ and $\Delta V_{C_{ij}}$ for each binary had been generalized by the authors. Two more empirical constants s and r for each mixture are needed to obtain the pseudocritical constants for the mixture.

Summary and Conclusions

1. An isothermal throttling calorimeter for direct determination of the effect of pressure on enthalpy was designed, fabricated, and tested. The recycle flow facility, as described by Bishnoi, was used to recycle the material for this study.

2. The effect of pressure on enthalpy was determined experimentally for nitrogen at temperatures from 0 to 100°C and pressures from 300 psia to 2000 psia. The data are in good agreement (within ± 1%) with other direct determinations in recent literature.

3. Measurement of the effect of pressure on enthalpy were made on 14.5 mole percent and 42.3 mole percent of methane in carbon dioxide at gas region at pressure from 300 to 2000 psia.

4. Skeleton enthalpy tables and enthalpy-pressure-temperature diagrams for those two mixtures were prepared, using isothermal enthalpy data of this work and isobaric heat capacity data of Bishnoi.

5. Measurements of the effect of pressure on enthalpy were also made on equimolal mixture of methane, carbon dioxide and nitrogen, equimolal mixture of methane, carbon dioxide and ethane, methane rich mixture of methane, carbon dioxide and ethane, and equimolal mixture of methane, carbon dioxide, nitrogen and ethane. The measurements are in gas region and pressure up to 2000 psia.

6. The data obtained in the course of this investigation plus data in the literature were used to compare several of the available methods of prediction. This comparative study indicates that corresponding states principle would be a most fruitful approach for extending methods of prediction.

7. A new recipe for obtaining pseudocritical parameters for the

mixture of the three parameter corresponding states correlation of Curl and Pitzer was developed to predict the isothermal enthalpy departure of mixture. In comparison with sixteen fluid compositions of experimental data in the literature, this new method gives lowest average absolute deviation among other methods of obtaining pseudocritical parameters.

Recommendations for Future Work

1. The pressure transducer for measuring the pressure drop across the calorimeter should be replaced by a more accurate and wider range pressure transducer.
2. The new device of flow meter should be developed in order to obtain more accurate experimental data.
3. The calorimeter should be modified in such a way that it would be easier to interchange the throttling coil.
4. A higher pressure drop throttling coil should be constructed in order to study the effect of pressure on enthalpy in liquid region and region across the two phases.
5. An oil and water removal unit should be installed at the outlet of the compressor in order to prevent the solid formation of oil or water which will plug the throttling unit of the calorimeter when operated at low temperature.

NOMENCLATURE

a_0, a_1, a_2, a_3	Constant in Equation (21)
a,b,c,d	Constant in BWR or BWRS equation of state
a,b	Constant in RK or SRK equation of state
A_0, B_0, C_0, D_0, E_0	Constant in BWR or BWRS equation of state
A,B	Calibration constants (flow meter)
B	Second virial coefficient in volume expansion
B'	Second virial coefficient in pressure expansion
B_R	Reduced second virial coefficient
B.P.	Normal boiling point
C	Third virial coefficient in volume expansion
C'	Third virial coefficient in pressure expansion
C_p	Isobaric heat capacity
D	Correlation term of Lydersen, Greenkorn, Hougen correlation
e	Base of natural logarithm
F	Mass flow rate
$\underline{H}$	Specific enthalpy
$\overline{H}$	Partial molal enthalpy
J,K	Expression in mixing rule of Joffe-Stewart, Burkhardt, Voo
K	Interaction constant for Barner and Quinlan mixing rule
k	Interaction constant
M	Molecular weight
m	Slope of $\alpha^{0.5}$ against $T_R^{0.5}$, Equation (85)
P	Pressure
P_C	Critical pressure

P_R	Reduced pressure P/P_C
ΔP	Pressure drop
$\dot{Q}$	Rate of heat transfer
q	Work per unit mass $\dot{W}/F$
R	Gas constant
r,s	Correction factor in mixing rule of Prausnitz and Gunn
T	Temperature
T_C	Critical temperature
T_R	Reduced temperature T/T_C
$\underline{V}$	Specific volume
$\dot{W}$	Rate of transfer of work
x	Mole fraction
y	Mole fraction
Z	Compressibility factor
α	Constant in mixing rule of Leland and Mueller
α,γ	Constant in BWR or BWRS equation of state
β,γ	Expression in mixing rule of Prausnitz and Gunn
Δ	Difference
μ	Joule-Thomson coefficient
μ'	Viscosity
ρ	Density
ψ	Dimensionless group of a thermodynamic property
θ,ν	Molecular shape factors
τ	Reciprocal of temperature 1/T
ω	Acentric factor
Ω_a,Ω_b	Parameter in RK or SRK equation of state
ϕ	Isothermal throttling coefficient

Subscripts

ad	Adiabatic condition
C	Critical point property
i,j	Component in a mixture
m	Mean value
m,mix	Mixture property
o	Zero pressure value
0	Reference substance property
1	Component 1
1	Inlet condition
11	Component 1
12	Interaction between component 1 and component 2
2,22	Component 2
2	Outlet condition

Superscripts

°	Zero pressure value
E	Excess property

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APPENDIX A

CALIBRATIONS AND ERROR ANALYSIS

TABLE XX

CALIBRATION DATA FOR 8163 MODEL PLATINUM RESISTANCE THERMOMETER

This thermometer was calibrated for use in the range 90.188 K < T < 773.15 K (-182.962°C < t < 500.60°C) on the International practical temperature scale of 1968.

For 13.81 K < T < 273.15 K

$$W = Wcct + dw$$

where W = R/R(0°C) and Wcct is a reference function, independent of any particular thermometer.

For 90.188 K < T < 273.16 K

$$dw = A4\ t + C4\ (t - 100)\ t^3$$

For 0°C < t < 630.74°C

$$t = t' + dt$$

where t' is determined by

$$w = 1 + At' + B(t')^2$$

and

$$dt' = 0.45(t'/100)\left(\frac{t'}{100} - 1\right)\left(\frac{t'}{419.58} - 1\right)\left(\frac{t'}{630.74} - 1\right)$$

The coefficient in the above relations were found by fixed-point calibrations, i.e. triple point of water, the steam of tin point and the zinc point using continuous thermometer currents of 1 and 2 mA.

TABLE XX (continued)

	0 mA	2 mA
A =	3.985566×10^{-3}	3.985539×10^{-3}
B =	-5.87663×10^{-7}	-5.87773×10^{-7}
A4 =	8.3280×10^{-7}	7.9460×10^{-7}
C4 =	2.2020×10^{-14}	2.4150×10^{-14}
R(0°C) =	25.5145 ohm	

TABLE XXI

CALIBRATION OF HIGH PRESSURE GAUGE

Manufacturer: Heise

Serial No.: H39686

Actual Pressure (psi)	Heise Gauge	
	up	down
0	0	0
200	200	200
400	400	400
600	596	600
800	796	800
1000	996	1000
1200	1200	1200
1400	1400	1400
1600	1600	1600
1800	1800	1806
2000	2000	2005
2200	2200	2205
2400	2400	2405
2600	2600	2605
2800	2800	2804
3000	3000	3000

A-4

TABLE XXII

CALIBRATION OF 250 PSI DIFFERENTIAL PRESSURE TRANSDUCER

Manufacturer: Validyne

psi	Voltage	
	up	down
0	0.001	0.004
30	1.169	1.191
50	1.956	1.976
70	2.741	2.760
80	3.135	3.161
100	3.925	3.951
120	4.717	4.743
140	5.514	5.541
160	6.316	6.339
180	7.122	7.144
200	7.936	7.952
220	8.752	8.766
240	9.577	9.582
250	9.992	9.992

TABLE XXIII

CALIBRATION OF 75 PSI DIFFERENTIAL PRESSURE TRANSDUCER

Manufacturer: Validyne

psi	Voltage (Volt)
0	0.001
10	0.654
20	1.311
30	1.971
40	2.635
50	3.303
60	3.976
70	4.656
75	4.999
70	4.657
60	3.980
50	3.310
40	2.642
30	1.979
20	1.318
10	0.658
0	0.001

TABLE XXIV

CALIBRATION OF 60 INS. OF WATER DIFFERENTIAL

PRESSURE TRANSDUCER

Manufacturer: Foxboro

Inches of Water	Voltage (mV)
0	0.983
4.293	1.275
8.945	1.597
12.541	1.841
17.752	2.184
20.209	2.352
25.041	2.676
30.70	3.059
35.70	3.399
40.37	3.713
45.45	4.057
50.05	4.363
60.27	5.055
54.60	4.671
48.55	4.263
31.39	3.105
22.043	2.477
18.354	2.225
14.150	1.194
11.310	1.747
7.313	1.476

TABLE XXV

FLOW METER CALIBRATION

(Orifice)

EQUATION: $$F = A + BY\sqrt{\frac{P \cdot \Delta P}{Z \cdot M}}$$

where

F: gm-mol min^{-1}

A, B: Calibration Constant

Y: $$\sqrt{\gamma^{2/k}\left(\frac{k}{k-1}\right)\left(\frac{1-\gamma^{(k-1)/k}}{1-\gamma}\right)\left(\frac{1-\beta^4}{1-\beta^4\gamma^{2/k}}\right)}$$

k: C_p/C_v

γ: $1 - \Delta P/P$

β: Ratio of orifice I.D. to tube I.D.

ΔP: Pressure drop across the orifice

P: Inlet-pressure of the orifice

Z: Compressibility factor of the gas (gas mixture)

TABLE XXV

P psia	ΔP psi	$Y\sqrt{\frac{P \cdot \Delta P}{Z \cdot M}}$	F	F_{cal}	$F-F_{cal}$
44.0600	1.8476	1.3873	4.8095	4.8107	-0.0012
44.1100	1.5086	1.2603	4.3566	4.3697	-0.0131
44.1100	1.2735	1.1616	4.0145	4.0275	-0.0130
44.1100	1.1880	1.1233	3.8783	3.8943	-0.0160
44.0100	0.7536	0.8989	3.0989	3.1156	-0.0167
44.1100	1.0314	1.0489	3.6234	3.6362	-0.0128
44.0100	0.3266	0.5952	2.0726	2.0618	0.0107
44.1400	0.7712	0.9105	3.1324	3.1559	-0.0235
44.1400	1.5615	1.2817	4.4199	4.4441	-0.0242
44.1900	1.2612	1.1573	4.0049	4.0124	-0.0075
44.1600	1.0469	1.0571	3.6544	3.6648	-0.0104
44.1600	0.5788	0.7910	2.7370	2.7414	-0.0044
44.1400	0.4266	0.6803	2.3446	2.3570	-0.0124
44.0100	0.2342	0.5046	1.7528	1.7474	0.0053
43.8700	0.2860	0.6607	2.2939	2.2892	0.0046
43.8700	0.3779	0.7586	2.6288	2.6289	-0.0001
43.8700	0.4917	0.8641	2.9967	2.9950	0.0016
43.8700	0.6184	0.9675	3.3570	3.3538	0.0031
43.8700	0.7413	1.0577	3.6774	3.6667	0.0106
43.8700	0.9240	1.1782	4.0825	4.0849	-0.0024
43.8700	1.0988	1.2819	4.4605	4.4450	0.0154
43.9100	1.5861	1.5315	5.3041	5.3109	-0.0068
43.9100	1.7790	1.6179	5.5864	5.6110	-0.0246
43.9100	1.5407	1.5102	5.2467	5.2373	0.0093
43.9100	0.9288	1.1817	4.0697	4.0972	-0.0275
43.9100	0.4239	0.8033	2.7951	2.7841	0.0109
43.9100	0.4426	0.8207	2.8506	2.8443	0.0062
43.9100	0.6237	0.9721	3.3938	3.3696	0.0241
43.9100	0.8364	1.1227	3.9297	3.8923	0.0373
43.9100	1.0149	1.2339	4.3044	4.2783	0.0260
43.9100	1.1971	1.3370	4.6666	4.6362	0.0303
43.9100	1.3558	1.4201	4.9209	4.9243	-0.0034
43.9100	1.5428	1.5112	5.2716	5.2407	0.0308
43.9100	1.5834	1.5302	5.3535	5.3066	0.0468
43.9100	0.1011	0.3940	1.3637	1.3636	0.0000
43.9100	0.1343	0.4538	1.5852	1.5710	0.0141
43.9100	0.2459	0.6133	2.1479	2.1245	0.0233
43.9100	0.1909	0.5407	1.8980	1.8726	0.0253
43.9100	0.3389	0.7191	2.5179	2.4917	0.0261
43.9100	0.2331	0.5972	2.0873	2.0686	0.0186
43.9100	0.2347	0.5992	2.0941	2.0757	0.0183
43.9100	0.2492	0.4957	1.7229	1.7166	0.0062
43.9100	0.3138	0.5559	1.9351	1.9252	0.0098
43.9100	0.4111	0.6353	2.2029	2.2011	0.0017
43.9700	2.2406	1.4474	5.0162	5.0191	-0.0029

TABLE XXV (continued)

P psia	ΔP psi	$Y\sqrt{\frac{P \cdot \Delta P}{Z \cdot M}}$	F	F_{cal}	$F-F_{cal}$
43.9700	2.2460	1.4490	5.0162	5.0247	-0.0085
43.9700	2.0846	1.3991	4.8654	4.8517	0.0136
43.9700	1.8618	1.3264	4.5785	4.5993	-0.0208
43.9700	1.6395	1.2486	4.3140	4.3291	-0.0151
43.9700	1.4188	1.1651	4.0276	4.0393	-0.0117
43.9700	1.2644	1.1022	3.8065	3.8211	-0.0146
43.9700	1.0811	1.0217	3.5360	3.5420	-0.0060
43.9700	0.9208	0.9450	3.2599	3.2758	-0.0159
43.9700	0.7589	0.8598	2.9649	2.9801	-0.0152
43.9700	0.6184	0.7776	2.6850	2.6948	-0.0098
43.9700	0.5174	0.7123	2.4418	2.4681	-0.0263
43.9700	0.4453	0.6614	2.2784	2.2915	-0.0131
43.9100	0.4490	0.6637	2.3055	2.2994	0.0060
43.9100	0.6750	0.8113	2.7892	2.8116	-0.0224
43.9100	0.8610	0.9139	3.1566	3.1677	-0.0111
43.9100	1.0768	1.0190	3.5360	3.5327	0.0032
43.9100	1.2778	1.1070	3.8289	3.8378	-0.0089
43.9100	1.6475	1.2506	4.3140	4.3361	-0.0221
43.9100	1.9275	1.3474	4.6891	4.6721	0.0169
43.9100	2.1274	1.4115	4.9146	4.8947	0.0198
44.2400	0.3945	0.7602	2.6380	2.6345	0.0034
43.7800	1.7865	1.5696	5.4560	5.4433	0.0126
43.7800	1.3953	1.3950	4.8305	4.8373	-0.0068
43.7800	0.8893	1.1217	3.8984	3.8889	0.0094
43.7800	0.5265	0.8675	2.9951	3.0067	-0.0116
43.7800	0.3854	0.7437	2.5586	2.5771	-0.0185
43.7800	0.2433	0.5920	2.0415	2.0508	-0.0093
43.7800	0.1663	0.4901	1.6862	1.6970	-0.0108

TOTAL SUM OF SQUARE = 0.97146E 03

SUM OF RESIDUAL = 0.28237E-05

SUM OF RESIDUAL SQUARE = 0.20049E-01

PERCENT STANDARD DEVIATION = 0.48473

STANDARD DEVIATION = 0.16804E-01

Y=A+B*X

A= -0.00391

B= 3.47033

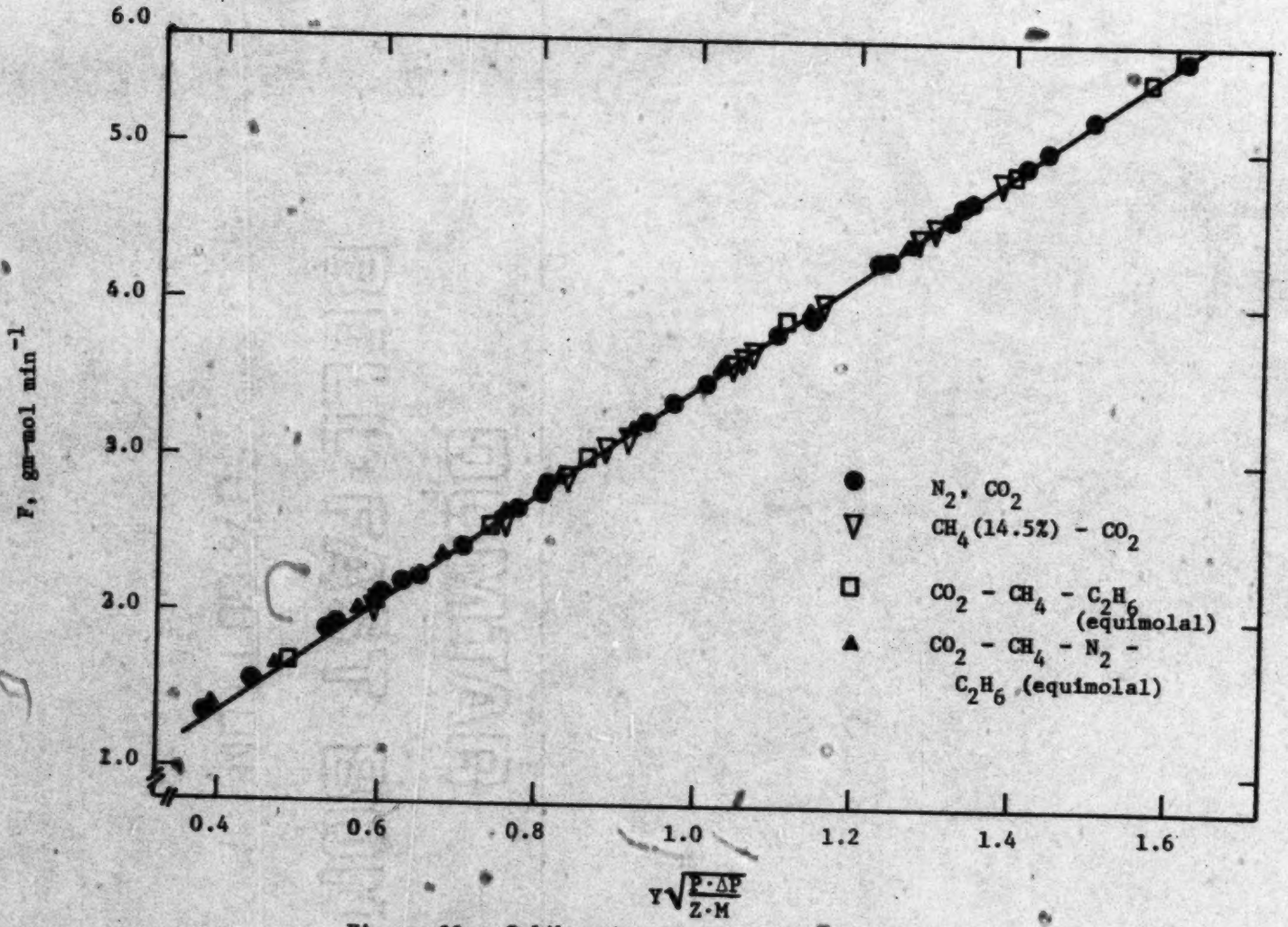

Figure 29: Calibration Curve of Orifice Meter

Calibration of Gas Chromatograph

1) Methane - Carbon Dioxide Mixtures

The binary mixtures of carbon dioxide and methane were analysed on a Burrell K-2 Kromo-tog Chromatograph using a three foot column of one-quarter inch diameter and packed with silica gel (40-100 mesh). A thermal conductivity detector was employed and helium was used as a carrier gas. Other variables were maintained at the following conditions:

Carrier gas flow rate	-	50 ml/min
Column temperature	-	80°F
Detector Current	-	150 mA
Sample size	-	2 ml

Excellent separations, with sharp well-defined peaks were obtained and the area under a peak was determined by a disc integrator. Standard sample mixtures of carbon dioxide and mixture were prepared by weighing small sample bottles and the amounts of methane and carbon dioxide charged. The weights of the empty bottle and the mixtures sample charged were approximately 155 g. and 1.75 g. respectively. The weighings could be reproduced to within ± 0.1 mg. The error in a mixture composition thus prepared should not exceed ± 0.2 percent. The standards were then analysed on the chromatograph and the area fraction of methane (area under a methane peak divided by the sum of the area under the carbon dioxide and methane peaks) was correlated to the known mole fraction of methane in the standards by the following functional relationship:

$$y = AX + BX^2$$

where A, B are constants

X = area fraction of methane

Y = mole fraction of methane

The constants, A and B, in the above relationship were determined by a least square fit and were found to be as follows:

A = 0.73451

B = 0.25721

The percent standard deviation of the fit was found to be ± 0.4%. A plot of Y versus X is shown in Figure 30.

2. *Methane, Carbon Dioxide and Ethane Mixture*

The mixtures were analysed on the same chromatograph using a one meter column of one-quarter inch diameter packed with porapak Type Q (80-100 mesh). The gas chromatograph was operated under the following conditions:

Carrier Gas	-	Helium
Carrier gas flowrate	-	40 ml/min
Column temperature	-	80°F
Detector current	-	170 mA
Sample size	-	2 ml

Standard mixtures of methane - carbon dioxide - ethane were prepared in the same method as for binary mixtures. The standards were then analysed on the gas chromatograph and the area fraction of each component were plotted against its more fraction as shown in Figure 31. A straight line was drawn through each component. The response factors of each component were then determined from the calibration curve by

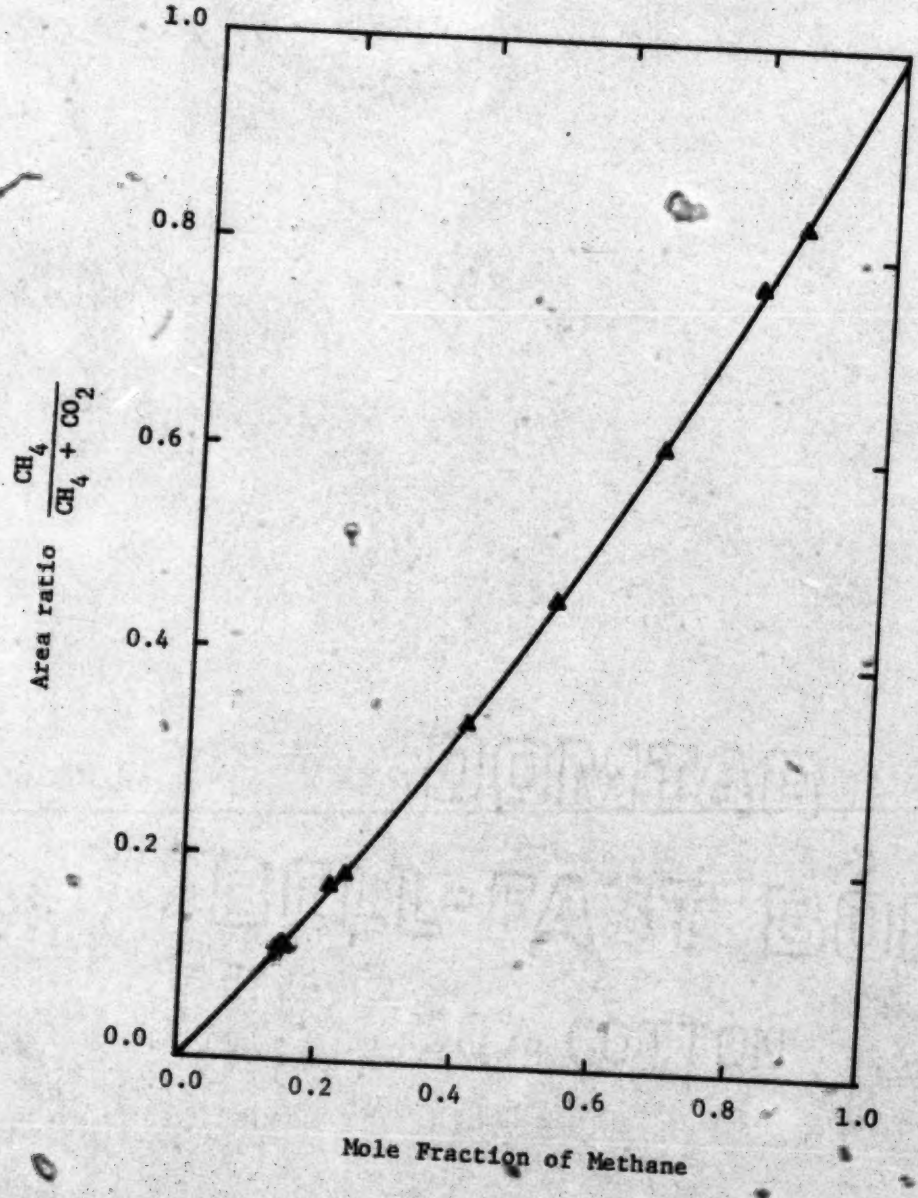

Figure 30: Gas Chromatograph Calibration for Methane-Carbon Dioxide Mixture

TABLE XXVI

RESPONSE FACTOR CALCULATED FROM CALIBRATION

Methane - Carbon Dioxide - Ethane System:

CH_4	:	36
CO_2	:	49
C_2H_6	:	53.5

Methane - Carbon Dioxide - Nitrogen System:

CH_4	:	36
N_2	:	41.8
CO_2	:	49

Methane - Carbon Dioxide - Nitrogen - Ethane System:

CH_4	:	36
N_2	:	41.7
CO_2	:	48.6
C_2H_6	:	54.5

assigning the response factor of methane equal 36. The calibrated response factors were listed in Table XXVI.

3. Methane - Carbon Dioxide - Nitrogen Mixture

The same gas chromatograph with same conditions and same procedure of the previous ternary system were used to calibrate mixture of this system. Figure 32 shows the area fractions of each component plotted as function of its mole fraction, and the calibrated response factors are listed in Table XXVI.

4. Methane - Carbon Dioxide - Nitrogen - Ethane Mixtures

The same gas chromatograph with same operating conditions and same procedure of the previous ternary system were used to calibrate mixture of methane - carbon dioxide - nitrogen - ethane system. Figure 33 shows the calibration curve and the response factors are listed in Table XXVI

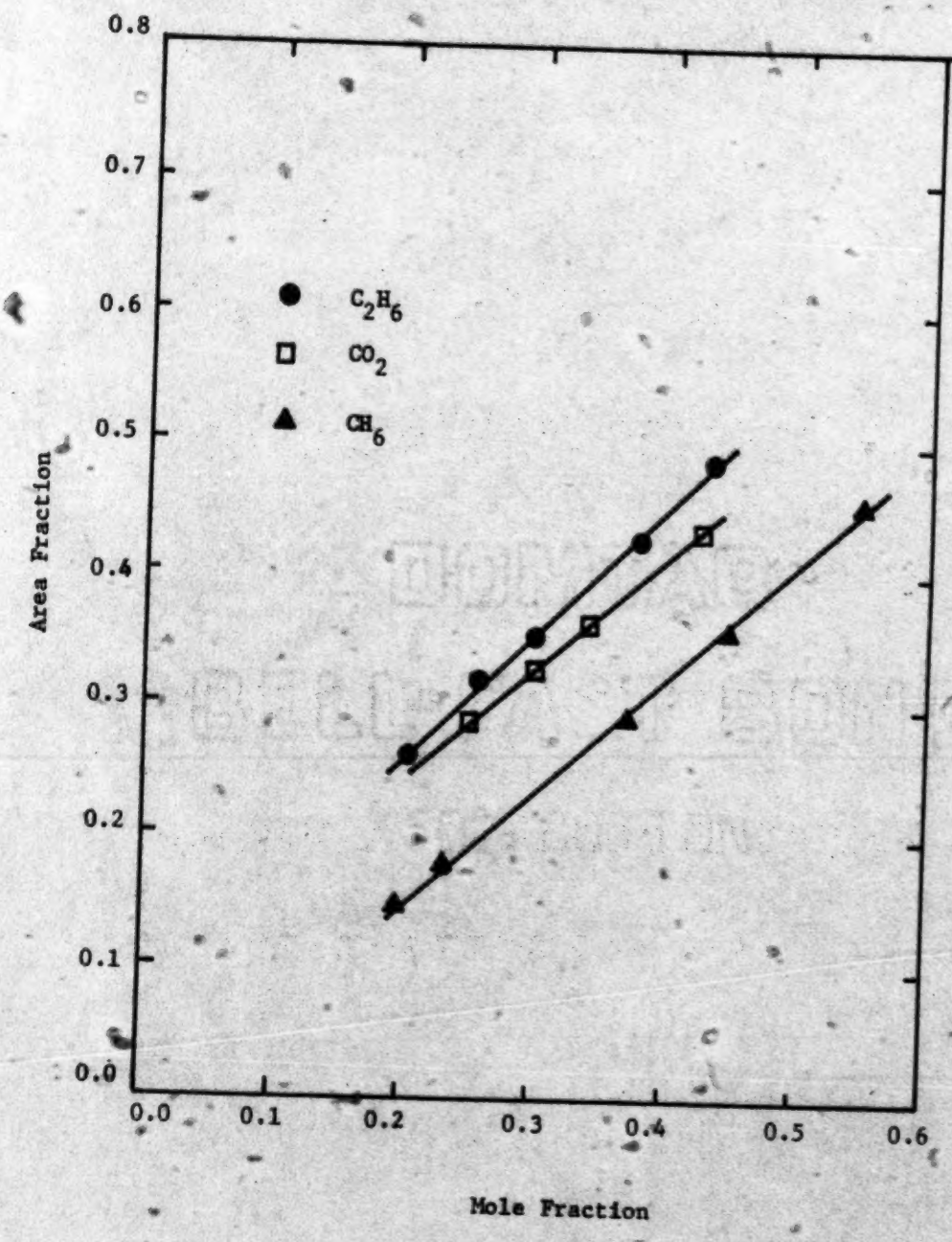

Figure 31: Gas Chromatograph Calibration for CH_4-CO_2-C_2H_6 Mixture

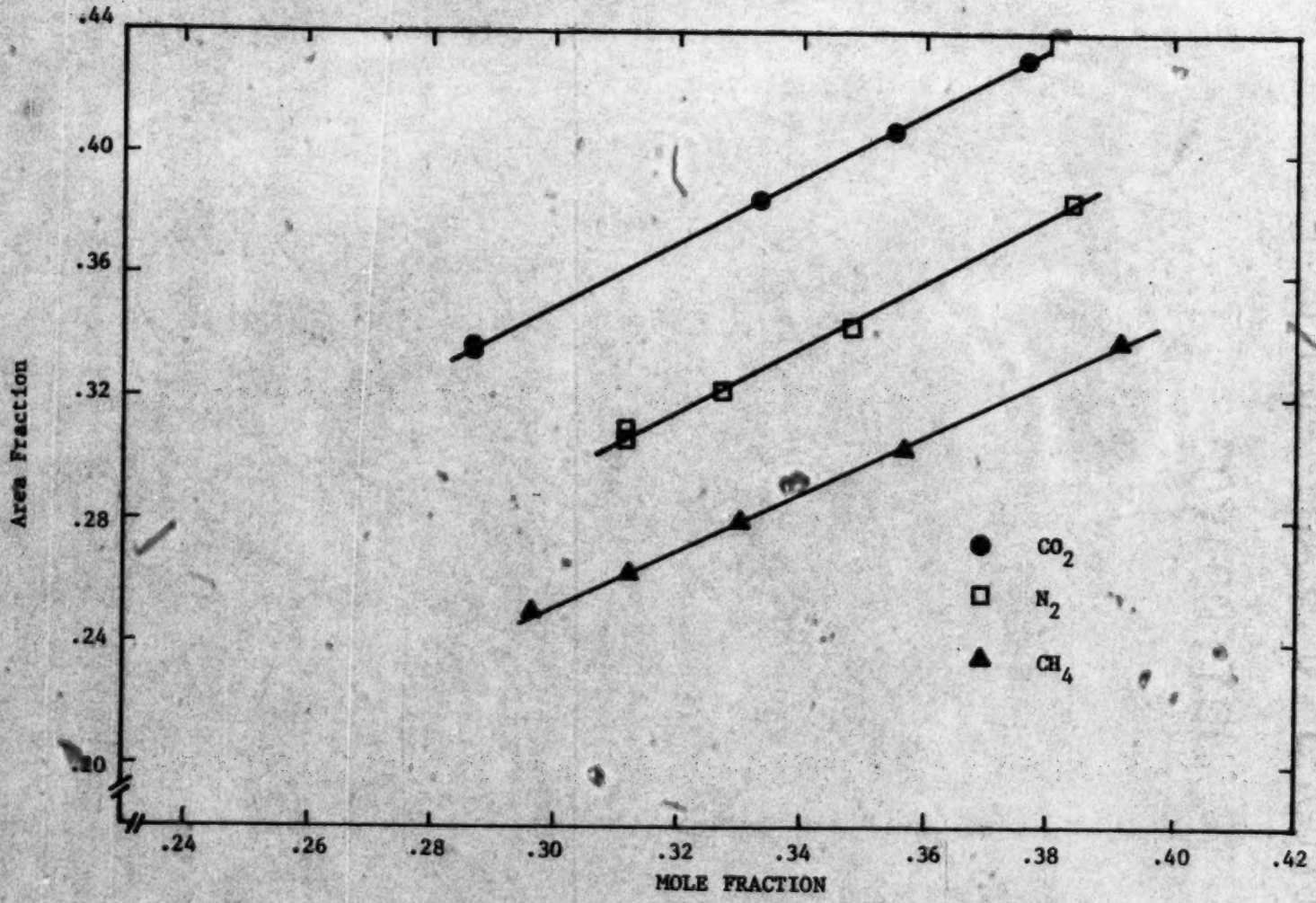

Figure 32: Gas Chromatograph Calibration for CO_2-CH_4-N_2 Mixture

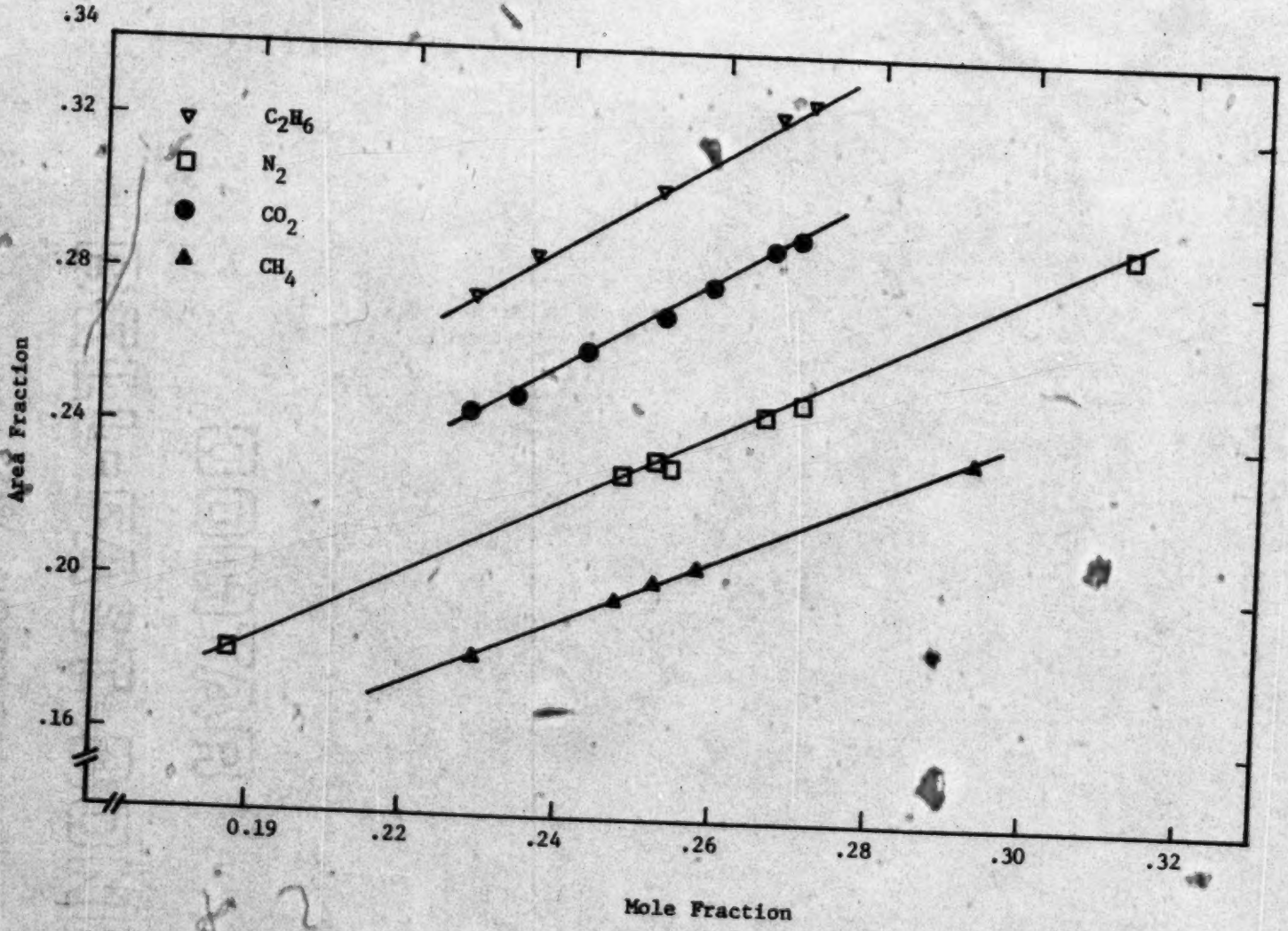

Figure 33: Gas Chromatograph Calibration for CH_4-CO_2-N_2-C_2H_6 Mixture

Error Analysis

The desired values of the isothermal throttling coefficient is determined from the results of measurement:

$$\phi_m = \left(\frac{\Delta H}{\Delta P}\right)_T = -\frac{\dot{W}}{\Delta P \cdot F} \tag{A1}$$

where $\dot{W}$ = power supply

F = mass flow rate

ΔP = pressure drop across the throttling unit

The maximum relative error of ϕ_m in the experiment is

$$\frac{\Delta\phi}{\phi} = \frac{\Delta\dot{W}}{\dot{W}} + \frac{\Delta(\Delta P)}{\Delta P} + \frac{\Delta F}{F} + \frac{1}{\phi}\left[\left(\frac{\partial\phi}{\partial P}\right)_{T,x}\Delta P_m + \left(\frac{\partial\phi}{\partial T}\right)_{P,x}\Delta T_m + \left(\frac{\partial\phi}{\partial x}\right)_{P,T}\Delta x\right] \tag{A2}$$

where ΔT_m = error in the measurement of inlet temperature of the gas in the calorimeter

ΔP_m = error in the measurement of the system pressure P_m

Δx = error in the measurement of composition in the mixture

Clearly,

$$\frac{\Delta\dot{W}}{\dot{W}} = \frac{\Delta\dot{W}_H}{\dot{W}_H} + \left(\frac{\Delta\dot{W}}{\dot{W}}\right)_{rel} + \frac{\dot{W}_{loss}}{\dot{W}} \tag{A3}$$

where $\Delta\dot{W}_H/\dot{W}_H$ = calculated error of measurement of the compensating power of the calorimeter heater; $(\Delta\dot{W}/\dot{W})_{rel}$ = error in the value of the compensating power, due to the non-zero value of the temperature difference between the inlet and outlet; $\Delta\dot{W}_{loss}/\dot{W}$ = error connected with spurious heat transfer between the calorimeter and the thermostat.

In this experiment, a Hewlett-Packard Model 3450 multifunction meter is used for all electrical measurements. For $\dot{W} = IV$, the measurement of current I is by means of measuring the voltage drop across a standard resistor, the uncertainty of voltage is about ± 5 microvolt. So the term $(\Delta\dot{W}/\dot{W})_H = \pm(0.005 - 0.002)$ %. The term $(\Delta\dot{W}/\dot{W})_{rel}$ can be replaced by the ratio $\Delta T_i/\Delta T_{ad}$, where ΔT_i = the degree of non-isothermal state of the inlet and outlet of the gas when the calorimeter is in operation; ΔT_{ad} = degree of non-isothermal state when no heat is added. The deviation of null meter which is used for the measurement of the output of the five junction thermopile is about ± 2 μV which is equivalent to 0.01°C, then

$$\frac{\Delta T_i}{\Delta T_{ad}} = \frac{\pm 0.01}{\Delta T_{ad}} = \frac{\pm 1}{\Delta T_{ad}} \%$$

For nitrogen: $0.1\% < (\Delta\dot{W}/\dot{W})_{rel} < 0.35\%$

For CH_4(43.3%)-CO_2: $0.03\% < (\Delta\dot{W}/\dot{W})_{rel} < 0.1\%$

For Equimolal CO_2-CH_4-C_2H_6: $0.03\% < (\Delta\dot{W}/\dot{W})_{rel} < 0.1\%$

The term $(\dot{W}_{loss}/\dot{W})$ is minimized by using the radiation shield surrounding the throttling unit and the calorimeter is evacuated to about 5 microns. This term can be neglected. The error in determining ΔP and F are:

for $\frac{\Delta(\Delta P)}{\Delta P} = \pm 0.5\%$

and for (ΔF/F):

$(\Delta F/F) \leq \pm 0.8\%$ for nitrogen

$\leq \pm 1.0\%$ for 42.3% CH_4 in CO_2 mixture

$\leq \pm 0.5\%$ for other mixtures

so, the maximum systematic error without the related error i.e. without allowing for the last term in Equation (A2) is

$\pm 0.5 \leq \varepsilon \leq \pm 1.4$ for nitrogen

$\pm 0.5 \leq \varepsilon \leq \pm 1.6$ for 42.3% methane in CO_2 mixture

$\pm 0.5 \leq \varepsilon \leq \pm 1.1$ for other systems

The temperature of the gas in the calorimeter is measured with an error of less than ±0.01°C, i.e. $\Delta T_m = 0.01°C$. The test value ϕ are related to the pressure $P_m = P_1 - (\Delta P/2)$ and the inaccuracy of determining the pressure is taken as ±1.0 psi (the resolution of the Heise gauge). The term $\frac{1}{\phi} [(\frac{\partial \phi}{\partial P})_{T,x} \Delta P_m] = \varepsilon_1$ will be,

$\pm 0.0003 \leq \varepsilon_1 \leq 0.002\%$ for nitrogen

and $\pm 0.0005 \leq \varepsilon_1 \leq 0.15\%$ for 42.3% CH_4 in CO_2 mixture. The term $\frac{1}{\phi} [(\frac{\partial \phi}{\partial T})_{P,x} \Delta T_m] = \varepsilon_2$, will be less 0.1% for methang-carbon dioxide mixtures.

APPENDIX B

ENTHALPY FORMULAE AND LOOP CHECKS

I. FORMULAE USED IN CALCULATION OF PROPERTIES FROM EQUATIONS OF STATE

1. Benedict-Webb-Rubin Equation

a) Enthalpy Departure

$$(\underline{H}_P - \underline{H}_o)_T = (B_0RT - 2A_0 - \frac{4C_0}{T^2})\rho + (bRT - \frac{3a}{2})\rho^2 + \frac{6a\alpha\rho^5}{5}$$

$$+ \frac{c\rho^2}{T^2}\left[\frac{3(1 - e^{-\gamma\rho^2})}{\gamma\rho^2} - \frac{e^{-\gamma\rho^2}}{2} + \gamma\rho^2 e^{-\gamma\rho^2}\right]$$

b) Isothermal Throttling Coefficient

$$\phi = \frac{(B_0RT - 2A_0 - \frac{4C_0}{T^2}) + (2bRT - 3a)\rho + 6a\alpha\rho^4 + \frac{ce^{-\gamma\rho^2}}{T^2}[5\rho + 5\gamma\rho^3 - 2\gamma^2\rho^5]}{RT + 2\rho(B_0RT - A_0 - \frac{C_0}{T^2}) + 3\rho^2(bRT - a) + 6a\alpha\rho^5 + \frac{ce^{-\gamma\rho^2}}{T^2}[3\rho^2(1 + \gamma\rho^2) - 2\gamma^2\rho^6]}$$

2. Soave-Redlich-Kwong Equation

a) Enthalpy Departure

$$(\underline{H}_P - \underline{H}_o)_T = P\underline{V} - RT + \frac{T\frac{da}{dT} - a}{b} \ln \frac{\underline{V} + b}{\underline{V}}$$

b) Isothermal Throttling Coefficient

$$\phi = \underline{V} - T\frac{\left[\frac{R}{\underline{V} - b} - \frac{(\frac{da}{dT})}{\underline{V}(\underline{V} + b)}\right]}{\left[\frac{RT}{(\underline{V} - b)^2} - \frac{a(2\underline{V} + b)}{\underline{V}^2(\underline{V} + b)^2}\right]}$$

3. *Starling Benedict-Webb-Rubin Equation*

a) Enthalpy Departure

$$\left(\frac{H_P - H_o}{RT}\right)_T = \left(B_0 RT - 2A_0 - \frac{4C_0}{T^2} + \frac{5D_0}{T^3} - \frac{6E_0}{T^4}\right)\rho + \frac{1}{2}\left(2bRT - 3a - \frac{4d}{T}\right)\rho^2 + \frac{1}{5}\alpha\left(6a + \frac{7d}{T}\right)\rho^5 + \frac{c\rho^2}{\gamma T^2}\left[3 - \left(3 + \frac{1}{2}\gamma\rho^2 - \gamma^2\rho^4\right)\exp\left(-\gamma\rho^2\right)\right]$$

b) Isothermal Throttling Coefficient

$$\phi = \frac{1}{\rho} - T\left[\frac{\rho\left[R + \left(B_0 R + \frac{2C_0}{T^3} - \frac{3D_0}{T^4} + \frac{4E_0}{T^5}\right)\rho + \left(bR - \frac{d}{T^2}\right)\rho^2 - \frac{\alpha d\rho^5}{T^2} - \frac{2c\rho^2}{T^3}\left(1+\gamma\rho^2\right)e^{-\gamma\rho^2}\right]}{\rho^2 T\left[R + \rho\left(2B_0 R - \frac{2A_0}{T} - \frac{2C_0}{T^3} + \frac{2D_0}{T^4} - \frac{2E_0}{T^5}\right) + 3\rho^2\left(bR - \frac{a}{T} - \frac{d}{T^2}\right) + 6\alpha\rho^5\left(\frac{a}{T} + \frac{d}{T^2}\right) + \frac{\left(3c\rho^2 + 3c\gamma\rho^4 - 2c\gamma^2\rho^6\right)}{T^3}e^{-\gamma\rho^2}\right]}\right]$$

II. THERMODYNAMIC CONSISTENCY CHECKS

The isothermal data of two mixtures of methane and carbon dioxide of this work were used in conjunction with isobaric data of Bishnoi to test the consistency of the experimental data. The location of the loops is shown in Figure 34 and 35. The enthalpy change along different paths are given in Table XXVII and XXVIII. The maximum deviation was 0.37 percent.

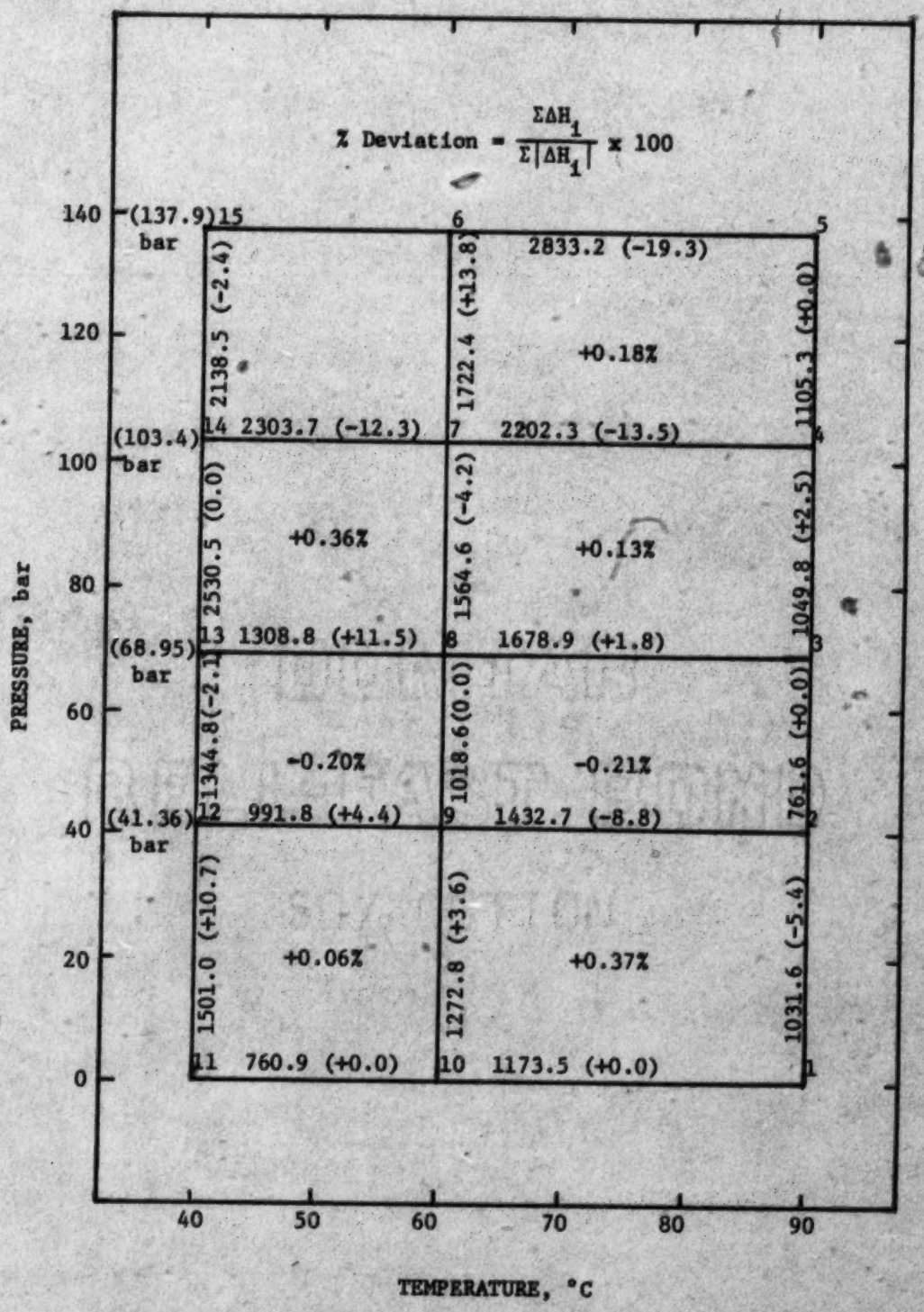

Figure 34: Location of Experimental Loops for 14.5 Percent Methane in Carbon Dioxide

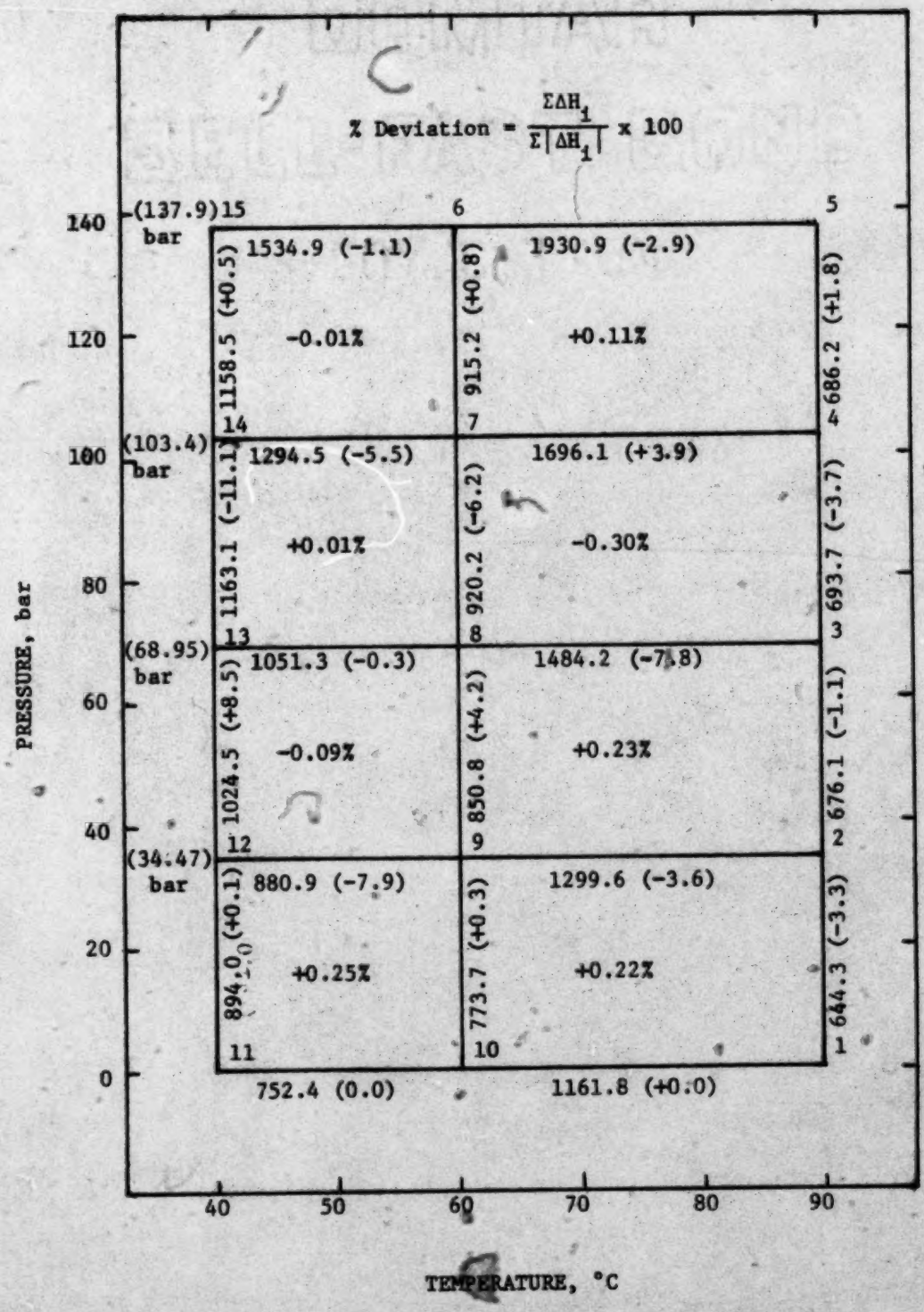

Figure 35: Location of Experimental Loops for 42.3 Percent Methane in Carbon Dioxide

TABLE XXVII

CONSISTENCY CHECKS ON THE MIXTURE OF 14.5 MOLE PERCENT METHANE IN CARBON DIOXIDE .

Loops	ΔH J mol^{-1}	% Deviation
1- 2- 9	+2464.3	
1-10- 9	-2446.3	+0.37
2- 3- 8	+2440.7	
2- 9- 8	-2451.3	-0.21
3- 4- 7	+3252.1	
3- 8- 7	-3243.5	+0.13
4- 5- 6	+3938.5	
4- 7- 6	-3924.7	+0.18
10- 9-12	+2264.6	
10-11-12	-2261.9	+0.06
9- 8-13	+2327.4	
9-12-13	-2336.6	-0.20
8- 7-14	+3867.3	
8-13-14	-3839.3	+0.36

TABLE XXVIII

CONSISTENCY CHECKS ON THE MIXTURE OF 42.3 MOLE PERCENT METHANE IN CARBON DIOXIDE

Loops	ΔH J mol^{-1}	% Deviation
1- 2- 9	+1943.9	
1-10- 9	-1935.5	+0.22
2- 3- 8	+2160.3	
2- 9- 8	-2150.4	+0.23
3- 4- 7	+2389.8	
3- 8- 7	-2404.4	-0.30
4- 5- 6	+2617.1	
4- 7- 6	-2611.3	+0.11
10- 9-12	+1654.6	
10-11-12	-1646.4	+0.25
9- 8-13	+1902.1	
9-12-13	-1905.4	-0.09
8- 7-14	+2214.7	
8-13-14	-2214.4	+0.007
7- 6-15	+2450.1	
7-14-15	-2453.0	-0.005

APPENDIX C

ISOTHERMAL THROTTLING COEFFICIENT

AT ZERO PRESSURE

TABLE XXIX

SECOND VIRIAL COEFFICIENT

T (K)	B, $cm^3\ mol^{-1}$				B_{12}, $cm^3\ mol^{-1}$					
	CO_2	CH_4	N_2	C_2H_6	CO_2-CH_4	CO_2-N_2	CO_2-C_2H_6	CH_4-N_2	CH_4-C_2H_6	N_2-C_2H_6
233.15	-262	-94.5	-29.0	-	-136.7	-95.1	-	-53.9	-	-
253.15	-180	-65	-15.5	-254	- 97.6	-68.9	-175	-33.4	-136	- 80
273.15	-150	-54	-10.5	-220	- 81.2	-57.3	-155	-26.7	-113	- 66
293.15	-127	-45	- 5.8	-192	- 67.3	-45.7	-133	-19.6	- 97	- 54.8
313.15	-110	-37.5	- 2.0	-166	- 57.3	-37.3	-113	-15.1	- 84	- 45.2
333.15	- 95	-31.5	1.0	-145	- 48.5	-30.5	- 96	-10.6	- 73	- 37.0
353.15	- 83.5	-26	3.8	-127	- 43.1	-25.1	- 83	- 7.14	- 64	- 29.9
373.15	- 73	-21	6.0	-112	- 36.6	-20.7	- 73	- 5.14	- 56	- 23.8

SOURCES:

Pure B are from Dymond and Smith[24]

B_{12} for CO_2-N_2, CO_2-CH_4, and CH_4-N_2 are from Ng[63]

B_{12} for CO_2-C_2H_6 is from Ng and Mather[64] and Zaalishvili[101]

B_{12} for CH_4-C_2H_6 is from Hoover[31], Gunn[27] and Dantzler *et al*[20]

B_{12} for N_2-C_2H_6 is from Pitzer and Curl Correlation[70]

TABLE XXX

ϕ° From Second Virial Coefficient

$$\phi^\circ = B_m - T \frac{dB_m}{dT}$$

T (K)	B_m ($cm^3 mol^{-1}$)	$\frac{dB_m}{dT}$ ($cm^3 mol^{-1} K^{-1}$)	ϕ° ($J\ mol^{-1}\ bar^{-1}$)	B_m ($cm^3 mol^{-1}$)	$\frac{dB_m}{dT}$ ($cm^3 mol^{-1} K^{-1}$)	ϕ° ($J mol^{-1}\ bar^{-1}$)
	42.3% CH_4 in CO_2			14.5% CH_4 in CO_2		
273.15	-99.3	0.825	-32.46	-127.8	1.15	-44.23
283.15	-	-	-	-118.2	1.02	-40.92
293.15	-	-	-	-108.1	0.890	-36.79
313.15	-71.5	0.542	-24.10	- 93.38	0.72	-31.91
333.15	-61.	0.452	-21.30	- 80.37	0.59	-27.78
363.15	-49.5	0.364	-18.20	- 65.5	0.474	-23.81
	Equimolal CH_4 - CO_2 - N_2			Equimolal CH_4 - CO_2 - C_2H_6 - N_2		
243.15	-80.91	0.738	-26.03	-115.5	1.00	-35.90
263.15	-66.96	0.609	-22.8	- 97.0	0.825	-31.40
283.15	-54.88	0.514	-19.04	- 82.0	0.67	-27.20
303.15	-	-	-	- 69.5	0.55	-23.60
333.15	-	-	-	- 53.5	0.425	-19.87
	Equimolal CH_4 - CO_2 - C_2H_6			CO_2(0.25) - CH_4(0.5) - C_2H_6(0.25)		
263.15	-134.5	1.08	-41.8	-111.5	0.95	-36.2
273.15	-124.0	1.02	-40.2	-103.0	0.825	-32.8
293.15	-106.0	0.82	-34.6	- 88.0	0.683	-28.8
313.15	- 90.5	0.68	-30.4	- 75.0	0.567	-25.2
333.15	- 77.5	0.57	-26.8	- 64.0	0.48	-22.3
363.15	- 63.0	0.447	-22.6	- 51.5	0.373	-18.68

APPENDIX D

EXPERIMENTAL DATA

TABLE XXXI

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
TEMPERATURE (K) = 273.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
426.5	176.6	190.115	2.1936	86.666	7.117
607.5	201.4	282.256	2.9607	95.334	6.865
613.4	203.4	290.666	2.9842	97.400	6.945
813.4	205.0	339.198	3.6109	93.936	6.646
813.5	203.5	331.240	3.5841	92.419	6.586
1112.0	212.5	401.705	4.3842	91.625	6.253
1117.0	207.5	393.090	4.3947	89.445	6.252
1415.0	211.5	432.904	5.0767	85.272	5.847
1416.0	207.3	412.422	4.9977	82.520	5.773
1416.0	206.0	410.424	5.0208	81.743	5.755
1713.0	178.2	342.220	5.2161	65.607	5.339
1713.0	177.5	338.782	5.2024	65.119	5.321
1713.0	176.2	333.636	5.1748	64.473	5.307
2020.0	147.6	249.642	5.1748	48.241	4.740
2020.0	146.5	248.226	5.1470	48.227	4.774
2020.0	145.0	242.927	5.1190	47.455	4.746
2317.0	132.5	198.180	5.1748	38.297	4.192
431.5	173.0	189.505	2.1964	86.276	7.233
431.5	172.9	187.716	2.2049	85.133	7.141
431.5	172.7	188.537	2.1964	85.836	7.208
431.5	172.6	191.484	2.2106	86.620	7.278
431.5	172.6	186.866	2.2021	84.856	7.130
618.5	188.0	259.678	2.9374	88.403	6.820
618.5	187.0	255.522	2.9327	87.127	6.757
618.5	184.9	252.217	2.9163	86.483	6.783
813.5	186.5	293.902	3.4953	84.085	6.539
813.5	184.7	289.751	3.4748	83.385	6.547
1107.0	185.0	328.327	4.1731	78.675	6.168
1107.0	183.8	326.156	4.1731	78.155	6.167
1414.0	186.3	355.320	4.8055	73.938	5.756
1714.0	186.2	557.066	5.3453	104.214	8.117
1714.0	185.8	356.000	5.3453	66.599	5.198
1714.0	185.7	357.251	5.3453	66.833	5.219
1714.0	185.5	352.784	5.3320	66.163	5.173
2014.0	164.9	293.360	5.4640	53.689	4.722
2014.0	164.0	289.930	5.4588	53.112	4.697
2014.0	162.6	287.597	5.4301	52.963	4.724
2304.0	143.7	225.535	5.4562	41.335	4.172
2304.0	143.0	222.120	5.4379	40.846	4.142
2304.0	142.3	220.159	5.4248	40.583	4.136

TABLE XXXI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
TEMPERATURE (K) = 303.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
415.3	178.0	139.891	2.0399	68.576	5.587
425.3	182.0	149.643	2.0838	71.810	5.722
463.5	198.1	178.370	2.2331	79.874	5.845
463.5	197.0	175.081	2.2998	76.127	5.604
815.3	215.1	273.546	3.5260	77.578	5.229
615.3	208.0	225.506	2.8728	78.496	5.473
616.0	249.0	292.125	3.1245	93.493	5.445
619.5	211.5	230.857	2.9280	78.842	5.406
619.5	207.0	223.696	2.8093	79.626	5.579
619.5	206.9	222.568	2.8093	79.224	5.553
815.0	229.5	301.703	3.6452	82.766	5.230
817.0	232.2	305.814	3.6784	83.137	5.191
1115.0	204.8	287.775	4.1685	69.034	4.887
1117.3	212.5	304.097	4.2306	71.879	4.906
1412.0	223.5	348.631	4.9740	70.089	4.548
1415.3	206.4	308.324	4.7696	64.642	4.542
1715.3	198.7	299.385	5.2362	57.175	4.172
1719.4	183.5	264.414	5.0426	52.436	4.144
2018.4	149.2	192.258	4.9691	38.690	3.759
2021.3	152.3	197.369	4.9897	39.554	3.766
2353.3	122.7	135.247	4.8283	28.011	3.309
2413.4	107.7	108.010	4.5983	23.489	3.161

TABLE XXXI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
TEMPERATURE (K) = 343.45

PI PSIA	ΔP PSI	POWER J/MIN	FLOW MOL/MIN	ΔH J/MOL	-(ΔH/ΔP) J/MOL-BAR
433.6	195.2	116.445	2.0103	57.923	4.302
437.7	194.2	115.902	2.0282	57.143	4.266
437.7	193.7	115.608	2.0282	56.998	4.266
437.8	197.2	119.322	2.0521	58.145	4.276
618.6	205.4	153.454	2.6657	57.564	4.064
618.8	213.5	163.650	2.7233	60.092	4.082
619.7	213.0	161.977	2.7095	59.780	4.070
619.7	212.5	160.043	2.7095	59.066	4.031
619.7	212.7	160.764	2.7095	59.332	4.045
619.7	212.7	161.977	2.7095	59.780	4.076
814.8	212.2	184.680	3.2676	56.517	3.862
821.7	215.2	189.234	3.3061	57.236	3.856
818.6	225.6	201.634	3.3716	59.803	3.843
821.7	214.7	187.693	3.2954	56.955	3.846
1117.6	219.0	215.542	4.0098	53.753	3.558
1419.6	190.3	185.521	4.2858	43.287	3.299
1723.5	216.2	230.575	5.0837	45.355	3.042
2015.5	170.0	157.410	4.9053	32.089	2.737
2330.5	154.0	133.733	5.0421	26.523	2.497
2410.5	116.8	85.158	4.4146	19.289	2.394

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR NITROGEN
TEMPERATURE (K) = 374.15

PI PSIA	ΔP PSI	POWER J/MIN	FLOW MOL/MIN	ΔH J/MOL	-(ΔH/ΔP) J/MOL-BAR
437.8	206.3	97.202	1.9710	49.315	3.467
438.8	200.0	91.735	1.9557	46.904	3.401
438.8	199.5	90.746	1.9557	46.398	3.373
438.8	199.5	89.227	1.9557	45.622	3.316
623.8	210.5	120.692	2.5715	46.933	3.233
819.8	210.0	136.690	3.0971	44.133	3.047
1117.8	198.8	140.176	3.6508	38.395	2.800
1427.8	204.1	153.367	4.2426	36.149	2.568
1717.8	210.8	163.650	4.7643	34.349	2.363
1717.8	199.3	161.677	4.7519	34.023	2.475
2013.8	194.5	141.971	5.0038	28.372	2.115
2243.8	162.1	104.853	4.8254	21.729	1.944

TABLE XXXII

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR THE 14.5 MOLE PERCENT OF CH_4 IN CO_2
TEMPERATURE (K) = 363.15

PI PSIA	ΔP PSI	POWER J/MIN	FLOW MOL/MIN	ΔH J/MOL	-(ΔH/ΔP) J/MOL-BAR
463.6	194.5	599.291	1.7574	340.996	25.427
515.6	203.2	670.778	1.8832	356.175	25.416
611.6	197.0	768.228	2.1577	356.024	26.211
611.6	196.2	762.697	2.1497	354.778	26.219
613.6	181.7	664.204	2.0273	327.616	26.144
809.6	175.6	825.870	2.4907	331.578	27.386
813.6	182.5	845.143	2.4602	343.519	27.300
1012.0	174.2	994.177	2.8914	343.837	28.619
1012.0	172.5	946.085	2.7823	340.035	28.590
1212.0	162.6	1057.043	3.1641	334.067	29.798
1216.0	157.5	979.680	3.0210	324.286	29.862
1412.0	158.2	1165.951	3.4688	336.118	30.815
1406.0	138.7	928.892	3.1363	296.173	30.959
1406.0	130.4	847.899	3.0333	279.527	31.090
1612.0	145.2	1158.108	3.6477	317.483	31.712
1612.0	141.0	1109.409	3.5917	308.880	31.772
1612.0	91.5	567.449	2.7933	203.146	32.201
1818.0	140.0	1211.007	3.9045	310.154	32.131
1994.0	118.0	1001.584	3.8234	261.961	32.198
2020.0	125.2	1098.551	3.9755	276.330	31.998

TABLE XXXII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 14.5 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 313.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
415.6	169.8	692.946	1.6171	428.501	36.601
605.6	184.5	1134.688	2.2090	513.666	40.380
605.6	184.0	1130.029	2.2066	512.100	40.366
813.6	163.5	1368.037	2.6132	523.509	46.439
1010.0	143.4	1578.056	2.9236	539.746	54.591
1010.0	142.5	1567.262	2.9155	537.552	54.712
1214.0	134.0	2047.897	3.3280	615.335	66.602
1214.0	133.2	2031.559	3.3210	611.727	66.584
1310.0	128.8	2295.553	3.5142	653.212	73.556
1412.0	127.3	2671.699	3.7815	706.508	80.495
1412.0	126.5	2647.914	3.7736	701.683	80.451
1415.0	83.0	1450.356	3.0791	471.026	82.309
1524.0	106.1	2314.756	3.7154	623.000	85.163
1524.0	104.9	2279.477	3.7003	616.013	85.171
1611.0	115.6	2776.365	4.1741	665.140	83.452
1701.0	109.2	2422.618	4.3113	561.915	74.632
1701.0	108.2	2378.256	4.2854	554.960	74.390
1814.0	96.0	1699.500	4.2540	399.502	60.357
1915.0	102.9	1577.787	4.5818	344.354	48.536
1915.0	102.5	1570.591	4.5735	343.410	48.592
1915.0	101.2	1536.208	4.5553	337.233	48.331
2013.0	86.0	981.341	4.2963	228.412	38.521

TABLE XXXII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 14.5 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 333.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
513.6	215.5	931.854	1.9674	473.635	31.877
713.6	177.5	981.050	2.3166	423.471	34.602
915.6	157.4	1073.432	2.6157	410.375	37.814
915.6	156.5	1065.170	2.6118	407.829	37.796
1112.0	159.2	1376.845	3.0448	452.192	41.196
1112.0	158.9	1372.038	3.0414	451.107	41.175
1314.0	154.4	1639.549	3.4118	480.538	45.140
1314.0	154.0	1635.234	3.4099	479.550	45.164
1314.0	153.5	1626.892	3.4010	478.345	45.197
1512.0	136.5	1660.767	3.5912	462.452	49.137
1514.0	144.0	1798.145	3.7095	484.729	48.822
1514.0	142.4	1769.884	3.6826	480.600	48.950
1762.0	127.0	1770.634	3.9594	447.197	51.071
1762.0	128.0	1802.599	3.9817	452.714	51.297
1762.0	125.0	1730.858	3.9369	439.649	51.012
2012.0	102.8	1329.178	3.9817	333.816	47.097
2012.0	100.7	1290.213	3.9427	327.236	47.131

TABLE XXXII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 14.5 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 293.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
418.5	156.8	830.148	1.7112	485.108	44.871
418.5	156.2	825.384	1.7067	483.607	44.904
419.5	159.0	823.012	1.6562	496.904	45.327
420.5	160.8	840.886	1.6770	501.398	45.224
517.5	157.5	1036.280	1.9754	524.579	48.307
517.5	156.1	1027.045	1.9631	523.157	48.608
555.5	142.5	1028.620	2.0659	497.883	50.675
609.5	140.0	1142.614	2.1992	519.543	53.823
613.5	145.5	1158.057	2.1467	539.437	53.772
708.5	142.5	1470.338	2.4938	589.575	60.007
807.5	142.5	1807.548	2.6698	677.030	68.908
957.6	168.5	1827.272	1.7617	1037.166	89.275
959.5	143.9	2817.071	3.0885	912.089	91.930
959.5	141.3	2779.054	3.1005	896.305	92.001
959.5	139.9	2753.518	3.1081	885.899	91.843
1009.6	165.0	2243.140	1.9000	1180.577	103.774
1014.0	102.2	2359.670	2.9580	797.721	113.209
1054.0	128.0	2302.114	2.0906	1101.130	124.770
1052.0	101.6	2267.335	2.4770	915.342	130.668
1054.0	102.2	2250.984	2.4568	916.193	130.022
1108.0	102.4	3348.740	2.8421	1178.242	166.884
1108.0	101.5	3375.931	2.8942	1166.423	166.675
1108.0	101.2	3362.466	2.8777	1168.420	167.455
1156.0	93.5	4276.152	3.0768	1389.764	215.581
1204.0	87.1	4685.280	3.2941	1422.285	236.837
1204.0	84.4	4551.967	3.2967	1380.748	237.276
1234.0	86.0	5017.247	3.8250	1311.665	221.210
1262.0	80.5	4043.094	3.8155	1059.625	190.914
1262.0	80.0	4009.822	3.8311	1046.641	189.753
1298.0	84.6	3654.539	4.1202	886.974	152.062
1318.0	82.5	3054.063	4.1635	733.520	128.955
1318.0	82.0	3013.848	4.1525	725.776	128.372
1318.0	81.7	3000.119	4.1399	724.667	128.646
1318.0	80.5	2933.559	4.1051	714.607	128.751
1362.0	84.6	2367.385	4.3587	543.137	93.115
1614.0	95.7	951.568	5.0363	188.941	28.634
1614.0	95.2	939.028	5.0300	186.682	28.441
1614.0	94.0	920.727	5.0000	184.144	28.412
1464.0	83.0	1298.474	4.5320	286.509	50.065
1813.0	92.5	566.047	5.0858	111.298	17.451
1813.0	92.5	566.047	5.0889	111.231	17.440
2008.0	79.0	311.398	4.7829	65.105	11.952
2009.0	75.4	293.467	4.6643	62.916	12.102

TABLE XXXII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR THE 14.5 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 283.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
419.5	145.8	889.046	1.6090	552.526	54.963
419.5	145.6	887.201	1.6107	550.815	54.868
483.5	143.6	1036.845	1.7854	580.727	58.654
553.5	138.5	1191.556	1.9573	608.755	63.749
628.5	131.0	1366.217	2.1245	643.058	71.196
629.5	131.0	1367.535	2.1245	643.679	71.265
695.5	123.0	1529.424	2.2476	680.442	80.235
745.5	121.1	1772.513	2.3803	744.628	89.182
773.5	119.8	1955.877	2.4638	793.815	96.104
773.5	119.3	1944.557	2.4596	790.571	96.113
810.5	112.7	2129.922	2.5219	844.541	108.687
1246.5	100.5	1219.439	5.4257	224.750	32.435
1246.5	90.0	993.305	5.1261	193.771	31.226
1265.5	90.2	919.281	5.1564	178.276	28.666
1265.5	86.5	852.661	5.0463	168.967	28.331
1275.5	87.6	839.516	5.0833	165.149	27.343
1293.5	89.5	821.191	5.1534	159.347	25.822
1293.5	89.0	806.192	5.1504	156.528	25.508
1308.5	87.2	739.603	5.1017	144.969	24.112
1355.5	83.5	591.679	5.0245	117.758	20.454
1414.5	84.0	506.595	5.0864	99.597	17.196
1473.5	81.8	421.487	5.0419	83.596	14.822
1473.5	80.5	410.706	5.0026	82.098	14.791
1529.5	82.0	380.994	5.0864	74.903	13.248
1595.5	79.8	320.825	5.0431	63.615	11.562
1595.5	79.2	317.986	5.0214	63.326	11.596
1655.5	76.0	266.851	4.9362	54.060	10.316
1705.5	77.7	254.394	5.0182	50.693	9.462
1705.5	76.4	250.192	4.9806	50.233	9.536
1815.5	78.7	223.091	5.0956	43.780	8.068
1815.5	78.2	218.274	5.0772	42.991	7.973
1909.5	70.1	166.816	4.8295	34.541	7.146
2009.5	64.5	126.672	4.6552	27.210	6.118

TABLE XXXII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 14.5 MOLE PERCENT OF CH_4 IN CO_2
TEMPERATURE (K) = 273.15

PI	/ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
413.5	138.0	952.758	1.6319	583.803	61.357
413.5	137.5	941.973	1.6254	579.509	61.127
478.5	141.6	1214.074	1.8465	657.495	67.345
525.5	132.5	1302.969	1.9452	669.829	73.321
571.5	125.3	1424.137	2.0389	698.477	80.850
585.8	122.6	1464.387	2.0733	706.282	83.554
1051.0	89.5	1278.791	5.2261	244.688	39.652
1051.0	82.7	997.855	5.0250	198.575	34.825
1100.0	80.5	343.843	5.0062	68.682	12.374
1198.0	80.9	282.580	5.0623	55.819	10.007
1228.0	79.4	256.801	5.0125	51.231	9.358
1256.0	82.5	266.048	5.1299	51.862	9.117
1311.0	78.8	216.733	4.9365	43.903	8.080
1354.0	80.7	219.255	5.0932	43.048	7.736
1398.0	77.5	185.859	4.9999	37.172	6.956
1398.0	77.9	188.255	5.0125	37.556	6.992
1442.0	73.5	161.808	4.8786	33.166	6.544
1526.0	78.8	156.197	4.9873	31.318	5.764
1594.0	81.5	156.197	5.1771	30.170	5.369
1657.0	78.2	133.611	5.0809	26.296	4.877
1657.0	77.5	132.084	5.0561	26.123	4.888
1711.0	76.5	118.586	5.0281	23.584	4.471
1711.0	75.9	117.876	5.0094	23.530	4.496
1711.0	74.6	112.882	4.9684	22.719	4.417
1759.0	73.6	103.790	4.9410	21.005	4.139
1759.0	73.0	101.763	4.9173	20.694	4.111
1816.0	66.2	78.350	4.6995	16.671	3.652

TABLE XXXIII

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 42.3 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 363.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
431.4	183.8	434.626	1.8047	240.829	19.004
431.4	183.2	431.792	1.7982	240.114	19.009
429.4	183.0	429.602	1.8017	238.442	18.897
619.4	195.0	616.525	2.3833	258.683	19.240
815.4	176.8	653.316	2.7407	238.370	19.554
815.4	176.2	649.560	2.7356	237.442	19.544
1017.0	167.5	709.719	3.0831	230.192	19.932
1017.0	166.8	705.380	3.0761	229.302	19.938
1217.0	168.2	812.023	3.4885	232.768	20.071
1217.0	167.5	806.890	3.4760	232.128	20.099
1217.0	167.0	801.588	3.4677	231.157	20.075
1415.0	161.4	842.537	3.7612	224.007	20.129
1613.0	164.5	939.909	4.1129	228.522	20.148
1613.0	164.0	936.676	4.1094	227.932	20.157
1811.0	148.8	859.777	4.2041	204.508	19.933
1811.0	148.0	857.203	4.1971	204.233	20.014
2017.0	126.9	707.543	4.1517	170.418	19.477
2017.0	121.8	668.143	4.0738	164.009	19.530
2017.0	119.6	649.549	4.0197	161.589	19.595

TABLE XXXIII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 42.3 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 333.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
426.5	173.2	506.400	1.8583	272.492	22.818
619.5	190.5	781.843	2.5147	310.903	23.670
820.5	184.2	936.376	2.9990	312.228	24.584
820.5	183.6	931.765	2.9956	311.035	24.570
1015.0	170.8	1004.805	3.3490	300.031	25.477
1215.0	169.7	1154.349	3.7777	305.565	26.115
1215.0	169.2	1150.465	3.7661	305.476	26.185
1215.0	168.3	1140.957	3.7622	303.264	26.134
1215.0	167.2	1129.555	3.7544	300.854	26.097
1415.0	167.0	1276.662	4.1448	308.008	26.750
1415.0	166.0	1265.803	4.1360	306.040	26.739
1613.0	150.2	1202.488	4.2988	279.724	27.011
1613.0	149.5	1190.880	4.2886	277.683	26.939
1813.0	152.3	1309.613	4.6685	280.517	26.714
1813.0	150.5	1288.312	4.6405	277.620	26.754
2015.0	128.0	1045.762	4.5934	227.663	25.796
2015.0	117.4	913.316	4.4027	207.443	25.627

TABLE XXXIII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 42.3 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 313.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
427.4	166.5	583.498	1.9290	302.479	26.348
427.4	166.0	579.139	1.9224	301.248	26.320
427.4	165.8	577.903	1.9224	300.605	26.296
427.4	165.2	574.705	1.9158	299.971	26.336
615.4	183.0	906.149	2.5860	350.395	27.770
615.4	182.6	902.768	2.5807	349.807	27.784
615.4	182.5	899.968	2.5754	349.442	27.771
813.4	161.6	979.234	2.9702	329.680	29.589
813.4	161.4	978.313	2.9702	329.370	29.598
1017.0	148.0	1070.568	3.3488	319.677	31.327
1217.0	145.9	1253.064	3.7766	331.791	32.983
1417.0	144.3	1431.353	4.1623	343.884	34.564
1617.0	134.0	1435.355	4.4429	323.060	34.967
1617.0	132.2	1402.092	4.4023	318.488	34.941
1715.0	126.8	1367.427	4.5110	303.128	34.672
1715.0	126.0	1356.272	4.4917	301.949	34.757
1715.0	124.5	1330.150	4.4658	297.852	34.698
1815.0	127.4	1403.239	4.7025	298.399	33.971
1815.0	126.8	1392.201	4.6902	296.828	33.952
1815.0	126.4	1383.312	4.6871	295.126	33.864
1815.0	124.3	1352.728	4.6500	290.904	33.943
2021.0	103.7	1028.901	4.5874	224.285	31.369
2021.0	102.7	1010.614	4.5621	221.521	31.284
2021.0	102.0	1003.029	4.5440	220.733	31.387

TABLE XXXIII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
THE 42.3 MOLE PERCENT OF CH4 IN CO2
TEMPERATURE (K) = 273.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
424.6	147.5	791.026	2.0285	389.938	38.342
424.6	147.3	789.374	2.0285	389.124	38.314
615.6	157.2	1307.205	2.7481	475.668	43.886
815.6	157.0	1960.814	3.4177	573.713	53.000
815.6	157.5	1968.975	3.4177	576.100	53.051
1016.0	148.5	2782.203	4.0433	688.090	67.204
1016.0	147.7	2772.157	4.0266	688.457	67.604
1016.0	147.5	2760.099	4.0229	686.083	67.463
1118.0	134.4	3026.130	4.1836	723.315	78.056
1118.0	133.3	2993.958	4.1766	716.826	77.994
1118.0	132.5	2971.018	4.1766	711.333	77.864
1214.0	126.5	3331.837	4.3918	758.640	86.981
1214.0	124.5	3266.655	4.3751	746.632	86.979
1214.0	125.4	3290.013	4.3751	751.971	86.973
1322.0	114.8	3158.507	4.5260	697.853	88.166
1322.0	113.5	3128.260	4.5356	689.700	88.134
1322.0	113.0	3111.921	4.5356	686.098	88.062
1416.0	110.0	2795.069	4.7454	588.997	77.660
1418.0	109.3	2777.665	4.7454	585.330	77.671
1418.0	108.7	2757.898	4.7485	580.791	77.494
1514.0	101.5	2117.643	4.8746	434.415	62.075
1514.0	101.2	2106.894	4.8717	432.473	61.981
1612.0	111.0	1998.708	5.3951	370.462	48.406
1612.0	110.3	1972.888	5.3714	367.289	48.296
1714.0	99.0	1325.974	5.3501	247.836	36.308
1812.0	92.6	973.487	5.3736	181.159	28.374
1812.0	92.1	959.989	5.3603	179.092	28.203
1812.0	90.4	930.153	5.2828	176.068	28.248
1914.0	85.8	696.325	5.2867	131.710	22.264
1914.0	80.0	617.927	5.0575	122.178	22.150
2016.0	76.6	477.233	5.0143	95.173	18.020

TABLE XXXIV

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2
TEMPERATURE (K) = 283.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
416.4	199.5	441.619	1.6133	273.720	19.899
419.4	200.0	450.868	1.6249	277.459	20.121
522.4	209.0	574.881	1.9451	295.553	20.510
607.4	212.5	667.732	2.1783	306.529	20.921
721.4	192.0	661.506	2.3471	281.835	21.290
806.4	182.5	672.763	2.4837	270.866	21.526
1009.4	172.7	740.144	2.8157	262.857	22.075
1009.4	171.5	731.693	2.8108	260.311	22.014
1208.4	170.4	826.584	3.1564	261.869	22.289
1410.4	163.5	858.777	3.4302	250.355	22.208
1410.4	163.2	855.692	3.4235	249.941	22.212
1410.4	162.5	849.331	3.4182	248.470	22.177
1558.4	163.2	897.053	3.6563	245.341	21.803
1558.4	162.2	890.252	3.6451	244.229	21.838
1715.4	165.5	943.792	3.9134	241.163	21.134
1715.4	165.0	938.749	3.9111	240.016	21.097
1858.4	164.0	938.985	4.1022	228.897	20.243
1858.4	163.2	935.717	4.0934	228.589	20.315
2029.4	146.1	777.128	4.0857	190.204	18.882

TABLE XXXIV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2
TEMPERATURE (K) = 263.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
415.6	194.2	541.518	1.6735	323.575	24.166
563.6	216.0	799.529	2.1121	378.546	25.418
759.6	208.0	950.825	2.4959	380.944	26.563
759.6	206.0	945.096	2.4997	378.083	26.619
908.6	193.7	985.308	2.6657	369.619	27.676
908.6	191.4	975.728	2.6761	364.595	27.628
1017.6	176.6	1056.383	3.0580	345.445	28.370
1017.6	175.6	1051.193	3.0550	344.088	28.420
1059.6	194.8	1123.240	2.9281	383.604	28.561
1059.6	192.0	1107.195	2.9312	377.716	28.532
1205.6	195.5	1222.936	3.1178	392.231	29.098
1205.6	190.8	1194.714	3.1223	382.634	29.086
1309.6	170.0	1244.736	3.6045	345.319	29.461
1309.6	169.2	1229.464	3.5931	342.167	29.330
1363.6	183.0	1200.628	3.2596	368.331	29.192
1363.6	181.0	1183.325	3.2610	362.866	29.077
1506.6	152.5	1036.447	3.4354	301.693	28.693
1506.6	149.6	1108.530	3.7498	295.621	28.660
1506.6	146.3	1016.572	3.5172	289.028	28.653
1658.3	149.6	1128.871	4.0108	281.452	27.286
1658.3	148.8	1118.598	3.9995	279.679	27.260
1779.6	139.9	1009.040	4.0602	248.518	25.764
1909.6	132.5	918.665	4.1688	220.363	24.121
2013.6	136.3	896.962	4.3246	207.407	22.070
2013.6	135.1	882.717	4.3111	204.754	21.981

TABLE XXXIV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2
TEMPERATURE (K) = 243.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
418.3	185.5	665.239	1.7545	379.149	29.644
513.3	192.4	855.550	2.0720	412.899	31.125
604.3	174.5	881.086	2.2571	390.353	32.444
712.3	179.4	1103.229	2.5796	427.667	34.575
712.3	179.2	1103.721	2.5796	427.857	34.629
863.3	152.5	1103.743	2.7731	398.009	37.853
863.3	151.7	1094.312	2.7664	395.560	37.818
1004.3	156.0	1372.523	3.1506	435.632	40.502
1004.3	155.5	1365.143	3.1474	433.731	40.454
1109.3	158.1	1562.947	3.4032	459.249	42.130
1109.3	157.0	1552.092	3.4112	454.986	42.032
1109.3	156.3	1537.906	3.3898	453.682	42.099
1208.3	159.1	1689.764	3.5957	469.929	42.839
1208.3	156.7	1665.987	3.5970	463.154	42.868
1375.3	149.7	1642.378	3.8253	429.343	41.597
1559.3	142.3	1418.202	3.9931	355.160	36.199
1707.3	143.5	1282.090	4.2377	302.538	30.578
1707.3	142.5	1276.394	4.2377	301.194	30.655
1865.3	133.5	972.058	4.2619	228.077	24.778
1865.3	132.5	963.597	4.2755	225.373	24.669
2016.3	136.2	850.046	4.4720	190.079	20.241

TABLE XXXV

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) = 363.15

PI PSIA	ΔP PSI	POWER J/MIN	FLOW MOL/MIN	ΔH J/MOL	-(ΔH/ΔP) J/MOL-BAR
270.4	146.3	216.171	0.9227	234.268	23.224
372.4	196.5	417.219	1.3179	316.572	23.366
426.4	211.2	515.212	1.5023	342.932	23.550
520.4	219.0	635.649	1.7711	358.885	23.768
613.4	215.6	708.807	1.9757	358.758	24.134
713.4	218.2	812.725	2.2088	367.935	24.456
716.6	195.2	699.629	2.1125	331.184	24.607
903.6	214.0	948.509	2.5710	368.917	25.003
1107.6	215.8	1125.895	2.9639	379.858	25.530
1214.6	177.2	905.836	2.8686	315.767	25.845
1214.6	175.7	895.723	2.8591	313.285	25.861
1236.6	201.0	1101.612	3.0901	356.493	25.723
1253.6	191.0	1026.381	3.0397	337.653	25.640
1407.6	185.6	1071.682	3.2446	330.288	25.810
1413.6	191.0	1123.714	3.2943	341.105	25.902
1417.6	191.0	1122.845	3.3011	340.135	25.828
1413.6	172.7	968.771	3.1396	308.558	25.913
1458.6	165.5	925.215	3.1432	294.347	25.795
1611.6	164.6	968.889	3.3434	289.785	25.534
1618.6	172.2	1045.663	3.4323	304.645	25.659
1613.6	150.8	854.476	3.2039	266.698	25.650
1657.6	186.6	1182.802	3.6150	327.184	25.430
1814.6	129.4	708.324	3.2053	220.979	24.768
2031.6	111.6	577.409	3.1826	181.424	23.578

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) = 333.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
273.7	142.3	265.675	0.9754	272.357	27.759
322.7	164.6	375.110	1.1702	320.533	28.243
417.7	187.5	558.244	1.5061	370.651	28.671
515.7	189.8	677.809	1.7642	384.183	29.357
515.7	189.6	679.617	1.7616	385.785	29.511
715.7	196.0	942.049	2.2560	417.573	30.899
715.7	196.0	944.165	2.2566	418.396	30.960
912.7	199.1	1207.128	2.7070	445.912	32.483
912.7	197.3	1192.003	2.6935	442.548	32.532
1113.7	173.6	1193.501	2.9265	407.816	34.071
1319.7	164.6	1289.414	3.2200	400.431	35.284
1459.7	154.5	1263.842	3.3633	375.771	35.275
1459.7	153.2	1248.582	3.3525	372.428	35.258
1459.7	149.5	1202.081	3.3131	362.824	35.199
1459.7	142.8	1124.295	3.2355	347.483	35.292
1607.7	138.4	1131.518	3.4114	331.686	34.759
1607.7	139.5	1144.366	3.4285	333.770	34.702
1709.7	169.1	1573.905	3.9348	399.991	34.307
1709.7	164.2	1503.814	3.8719	388.389	34.306
1709.7	160.5	1447.880	3.8371	377.336	34.098
1815.7	142.8	1228.598	3.7628	326.506	33.162
2019.7	119.5	909.537	3.6942	246.202	29.881
2019.7	117.1	880.115	3.6551	240.788	29.823
2019.7	117.1	880.115	3.6526	240.950	29.843

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) = 313.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
273.3	129.4	278.467	0.9723	286.385	32.099
319.3	149.9	390.678	1.1670	334.763	32.390
420.3	171.6	603.941	1.5211	397.033	33.557
521.3	195.5	873.902	1.8788	465.115	34.506
521.3	195.1	872.234	1.8788	464.227	34.510
713.3	193.0	1174.692	2.3573	498.316	37.448
918.3	194.0	1557.478	2.8598	544.593	40.714
1113.3	191.1	1904.919	3.2926	578.532	43.908
1215.3	180.2	1945.115	3.4353	566.204	45.572
1313.3	168.0	1910.388	3.5354	540.348	46.649
1313.3	167.0	1892.159	3.5253	536.729	46.614
1413.3	157.2	1859.563	3.6338	511.736	47.214
1413.3	155.5	1826.869	3.6153	505.305	47.130
1413.3	154.2	1803.783	3.6017	500.802	47.104
1414.3	146.5	1672.413	3.5075	476.803	47.204
1414.3	142.3	1607.940	3.4613	464.544	47.348
1511.3	143.0	1688.840	3.6558	461.957	46.854
1511.3	141.7	1668.011	3.6411	458.096	46.888
1511.3	141.4	1652.738	3.6356	454.589	46.628
1661.3	134.4	1559.186	3.8199	408.166	44.047
1661.3	133.1	1534.189	3.7954	404.212	44.046
1795.3	145.4	1696.760	4.1944	404.526	40.351
1915.3	139.3	1478.298	4.2869	344.835	35.903
1915.3	135.4	1412.976	4.2277	334.212	35.800
2028.3	126.3	1160.603	4.2225	274.855	31.563

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) = 293.15

PI	ΔP	POWER	FLOW	ΔH	$-(\Delta H/\Delta P)$
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
269.5	131.6	344.346	1.0122	340.171	37.490
315.5	152.2	483.661	1.2128	398.765	38.000
365.5	175.6	676.531	1.4485	467.051	38.576
365.5	175.0	673.792	1.4437	466.712	38.680
419.5	179.3	799.318	1.6198	493.601	39.928
419.5	178.6	789.560	1.6164	488.439	39.665
613.5	181.6	1222.887	2.1853	559.593	44.692
613.5	181.0	1214.028	2.1810	556.614	44.602
815.5	184.5	1801.682	2.7519	654.700	51.466
1017.5	186.1	2589.961	3.3324	777.203	60.571
1017.5	185.2	2576.171	3.3310	773.379	60.566
1112.5	178.0	2790.391	3.4779	802.302	65.373
1112.5	176.5	2768.562	3.4870	793.962	65.243
1112.5	174.5	2741.524	3.4857	786.499	65.370
1215.5	152.7	2587.446	3.5088	737.400	70.040
1315.5	146.1	2657.803	3.6956	719.171	71.394
1415.5	127.6	2258.605	3.7911	595.754	67.717
1613.5	126.5	1870.031	4.2168	443.469	50.845
1613.5	126.3	1869.417	4.2157	443.433	50.922
1613.5	123.4	1796.158	4.1620	431.559	50.723
1817.5	119.4	1223.165	4.3916	278.520	33.832
1817.5	120.2	1232.599	4.4036	279.905	33.774
2021.5	117.8	839.696	4.5627	184.033	22.658
2021.5	110.4	761.704	4.4145	172.543	22.667

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) = 273.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
267.4	124.3	392.552	1.0333	379.889	44.326
275.6	129.0	422.358	1.0719	394.015	44.300
275.6	129.0	422.761	1.0719	394.391	44.342
314.4	144.3	565.733	1.2486	453.084	45.540
347.6	160.0	725.265	1.4099	514.380	46.627
368.4	166.0	805.086	1.4949	538.537	47.053
406.4	167.6	936.895	1.6590	564.712	48.869
406.4	167.1	929.545	1.6534	562.172	48.794
419.6	175.1	1006.886	1.6905	595.606	49.335
419.6	175.0	1011.034	1.6891	598.547	49.606
420.7	158.6	881.820	1.6309	540.666	49.443
614.6	179.0	1714.355	2.3176	739.700	59.935
614.6	178.1	1695.904	2.3076	734.900	59.847
613.4	165.5	1591.088	2.2501	707.108	61.968
715.4	160.1	1950.160	2.5297	770.889	69.836
718.6	163.9	2005.081	2.5502	786.221	69.574
718.6	163.5	2004.983	2.5502	786.182	69.740
814.6	148.4	2354.089	2.7393	859.354	83.988
814.6	147.7	2328.537	2.7276	853.682	83.829
819.4	144.6	2310.429	2.7375	843.988	84.654
853.6	144.5	2558.524	2.7980	914.387	91.779
853.6	143.5	2538.246	2.7939	908.468	91.820
856.4	129.6	2263.890	2.7090	835.663	93.520
987.4	175.5	5111.978	3.4635	1475.921	121.974
987.4	173.8	5081.935	3.4661	1466.150	122.351
987.4	172.8	5077.787	3.4778	1460.053	122.548
987.4	171.5	5047.374	3.4752	1452.386	122.828
987.4	159.0	4482.825	3.2918	1361.814	124.223
987.4	158.0	4444.522	3.2794	1355.261	124.407
987.4	138.5	3736.590	3.0717	1216.434	127.385
987.4	137.8	3729.116	3.0761	1212.257	127.593
1057.4	160.5	5491.198	3.5492	1547.132	139.808
1057.4	138.0	4528.551	3.3541	1350.136	141.899
1121.4	122.4	4020.247	3.5555	1130.686	133.980
1121.4	122.3	4006.903	3.5404	1131.756	134.217
1216.4	118.7	3271.451	4.0363	810.487	99.032
1216.4	116.4	3211.285	4.0560	791.722	98.651
1315.4	127.5	2581.864	4.5573	566.525	64.445
1315.4	127.3	2563.598	4.5516	563.226	64.170

TABLE XXXV (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) = 273.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
1412.4	125.0	1674.845	4.7000	356.348	41.347
1412.4	124.8	1668.690	4.6935	355.527	41.318
1613.4	119.0	851.603	4.7993	177.442	21.626
1613.4	117.2	827.367	4.7622	173.734	21.500
1613.4	116.6	825.183	4.7486	173.773	21.615
1817.4	120.2	567.961	4.9660	114.369	13.800
1817.4	119.7	567.961	4.9312	115.175	13.955
2033.6	106.1	323.877	4.9231	65.786	8.992
2033.6	105.8	323.877	4.9055	66.022	9.050

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-C2H6
TEMPERATURE (K) = 263.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
269.6	122.5	442.983	1.0631	416.653	49.331
269.6	122.1	437.882	1.0587	413.566	49.125
348.6	154.2	789.237	1.4263	553.309	52.043
349.6	155.7	808.389	1.4426	560.359	52.198
420.6	185.0	1256.314	1.7814	705.210	55.287
420.6	184.7	1249.514	1.7801	701.906	55.118
420.6	137.8	859.040	1.5899	540.304	56.868
517.6	173.4	1574.284	2.0747	758.797	63.468
517.6	172.8	1561.740	2.0668	755.599	63.420
517.6	172.5	1551.990	2.0635	752.105	63.236
620.6	209.4	2750.847	2.6055	1055.779	73.127
620.6	209.4	2750.005	2.6055	1055.456	73.104
620.6	144.0	1719.275	2.2386	767.998	77.353

TABLE XXXVI

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) = 363.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
317.5	172.0	275.140	1.1996	229.342	19.339
317.5	171.0	271.279	1.1952	226.963	19.250
317.5	170.0	268.864	1.1907	225.784	19.263
422.5	185.1	378.732	1.5232	248.635	19.482
614.5	203.8	574.947	2.0673	278.103	19.791
614.5	203.2	572.480	2.0661	277.080	19.777
614.5	202.7	569.316	2.0571	276.746	19.802
817.5	204.3	708.245	2.4847	285.036	20.235
1009.5	196.0	771.254	2.7998	275.461	20.383
1215.5	196.3	875.964	3.1595	277.242	20.484
1215.5	196.0	874.591	3.1595	276.807	20.483
1215.5	195.7	869.678	3.1579	275.395	20.431
1415.5	184.1	871.225	3.3760	258.063	20.330
1415.5	182.5	861.078	3.3607	256.218	20.362
1617.5	187.8	966.356	3.3221	290.883	22.464
1617.5	187.5	960.948	3.7086	259.111	20.043
1815.5	165.7	842.595	3.7504	224.665	19.665
1815.5	164.5	829.216	3.7354	221.986	19.572
2049.5	155.5	783.325	3.8998	200.860	18.734
2049.5	154.9	778.882	3.8933	200.056	18.731
2049.5	147.2	720.927	3.7937	190.028	18.723

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) = 333.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
269.5	141.8	230.901	1.0221	225.904	23.106
320.5	166.8	333.096	1.2385	268.948	23.385
428.5	192.6	512.868	1.6301	314.617	23.692
608.5	193.9	689.526	2.1132	326.290	24.406
608.5	193.1	685.149	2.1094	324.793	24.395
608.5	193.0	682.959	2.1119	323.373	24.301
819.5	193.0	867.583	2.5889	335.108	25.183
819.5	192.4	863.495	2.5869	333.789	25.162
1009.5	187.9	988.240	2.9498	335.013	25.859
1009.5	187.7	986.245	2.9472	334.636	25.857
1009.5	187.7	984.511	2.9463	334.148	25.820
1212.5	185.3	1112.773	3.3127	335.905	26.291
1315.5	163.0	977.478	3.2866	297.407	26.463
1315.5	162.4	970.033	3.2827	295.495	26.390
1415.5	166.0	1057.050	3.4798	303.760	26.540
1415.5	165.5	1047.206	3.4754	301.314	26.406
1565.5	161.0	1070.825	3.6664	292.062	26.310
1565.5	160.0	1056.108	3.6538	289.040	26.201
1565.5	158.6	1044.875	3.6398	287.069	26.252
1715.5	159.5	1095.808	3.8893	281.746	25.620
1715.5	159.4	1091.680	3.8919	280.497	25.522
1871.5	149.5	1013.855	3.9836	254.504	24.690
1871.5	148.0	1004.240	3.9631	253.392	24.832
1871.5	146.5	982.897	3.9413	249.383	24.689
1871.5	140.0	916.900	3.8524	238.001	24.656
2037.5	132.5	836.259	3.9498	211.720	23.175
2037.5	132.4	837.429	3.9490	212.058	23.230
2037.5	131.8	832.146	3.9426	211.065	23.226
2037.5	131.0	823.312	3.9309	209.442	23.188

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) = 313.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
321.4	162.3	383.445	1.2766	300.342	26.839
415.4	184.7	568.778	1.6322	348.454	27.362
421.4	187.4	588.981	1.6579	355.252	27.494
421.4	187.0	586.830	1.6579	353.955	27.452
421.4	186.6	582.791	1.6547	352.195	27.374
616.4	190.7	831.712	2.2109	376.185	28.610
813.4	195.5	1103.845	2.7243	405.181	30.059
1007.4	190.8	1303.296	3.1434	414.606	31.516
1007.4	190.3	1296.973	3.1401	413.027	31.479
1007.4	190.0	1288.975	3.1335	411.344	31.400
1109.4	166.1	1162.725	3.1582	368.158	32.147
1109.4	165.6	1153.219	3.1524	365.812	32.039
1216.4	158.7	1178.006	3.2958	357.425	32.665
1316.4	159.0	1259.920	3.4855	361.469	32.972
1413.4	154.1	1270.359	3.6156	351.355	33.069
1563.4	160.1	1429.210	3.9560	361.272	32.728
1563.4	159.8	1421.867	3.9534	359.650	32.642
1717.4	145.8	1270.973	4.0355	314.947	31.330
1717.4	145.2	1267.520	4.0266	314.779	31.442
1867.4	136.0	1138.564	4.1200	276.346	29.471
1867.4	132.7	1100.317	4.0767	269.898	29.499
1867.4	129.4	1056.330	4.0254	262.414	29.412
2039.4	119.4	891.980	4.0829	218.462	26.537
2039.4	117.8	876.605	4.0593	215.948	26.588
2039.4	116.9	863.854	4.0342	214.130	26.567

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) = 293.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
267.4	132.8	299.416	1.0623	281.839	30.781
327.4	159.0	456.306	1.3377	341.091	31.114
419.4	182.9	690.714	1.7116	403.527	31.999
419.4	182.7	719.774	1.7086	421.263	33.442
613.4	207.5	1184.079	2.4013	493.087	34.465
812.4	201.3	1526.031	2.9312	520.607	37.510
1010.4	185.0	1743.273	3.3389	522.105	40.932
1010.4	184.4	1734.217	3.3342	520.115	40.909
1212.4	174.7	1982.531	3.7502	528.633	43.887
1212.4	173.9	1971.079	3.7421	526.729	43.930
1312.4	161.0	1909.207	3.8391	497.302	44.799
1312.4	160.7	1900.309	3.8364	495.327	44.705
1413.2	156.8	1947.715	4.0255	483.834	44.754
1512.4	150.5	1892.049	4.1667	454.084	43.760
1512.4	150.0	1881.796	4.1582	452.548	43.757
1663.4	133.1	1556.252	4.2150	369.215	40.233
1663.4	132.7	1547.683	4.2066	367.915	40.212
1815.4	132.8	1450.446	4.4636	324.948	35.489
1815.4	131.3	1422.072	4.4433	320.048	35.353
1815.4	131.3	1420.996	4.4365	320.296	35.380
1815.4	127.8	1362.375	4.3851	310.677	35.258
2028.4	111.0	905.988	4.3598	207.803	27.152
2028.4	110.0	893.769	4.3413	205.875	27.145

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) = 273.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
273.5	129.8	367.182	1.1326	324.177	36.223
337.5	157.2	579.779	1.4409	402.352	37.122
337.5	156.6	572.060	1.4336	399.031	36.957
420.5	190.6	922.269	1.8427	500.473	38.083
420.5	190.5	928.260	1.8456	502.944	38.291
613.5	179.8	1315.568	2.4195	543.721	43.859
811.5	185.9	2010.733	3.0739	654.110	51.033
811.5	185.2	1997.355	3.0672	651.189	50.997
1013.5	183.2	2857.021	3.6993	772.295	61.142
1013.5	182.7	2843.097	3.6938	769.685	61.102
1115.5	171.5	3063.815	3.9089	783.796	66.285
1115.5	170.8	3048.990	3.8984	782.094	66.412
1215.5	147.4	2805.575	3.9607	708.346	69.699
1215.5	147.0	2792.617	3.9562	705.877	69.645
1325.5	154.2	3179.131	4.3694	727.581	68.435
1411.5	151.3	3028.045	4.6403	652.546	62.553
1411.5	150.7	3011.289	4.6263	650.904	62.644
1508.5	142.2	2486.370	4.7646	521.840	53.225
1508.5	141.3	2462.425	4.7488	518.525	53.224
1659.5	143.9	1976.639	5.1159	386.369	38.942
1821.5	123.5	1140.630	4.9633	229.808	26.988
1821.5	122.5	1125.146	4.9448	227.537	26.940
1821.5	119.1	1071.676	4.8740	219.871	26.775
2030.5	117.1	720.952	5.0297	143.336	17.753
2030.5	116.5	717.082	5.0204	142.833	17.782
2030.5	116.0	713.062	4.9986	142.649	17.835

TABLE XXXVI (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
MIXTURE OF CO2(.25)-CH4(.5)-C2H6(.25)
TEMPERATURE (K) = 263.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
267.7	124.5	381.051	1.1260	338.381	39.420
324.7	148.0	580.372	1.4111	411.287	40.305
423.7	158.3	841.294	1.7772	473.361	43.370
423.7	158.1	841.294	1.7811	472.332	43.330
615.7	170.1	1477.360	2.4644	599.478	51.115
615.7	170.0	1476.989	2.4644	599.327	51.132
815.7	170.2	2375.540	3.1337	758.048	64.598
815.7	171.0	2387.989	3.1370	761.214	64.564
912.7	151.7	2602.301	3.3041	787.589	75.300
912.7	151.0	2590.558	3.3017	784.595	75.361
1009.7	161.0	3600.626	3.7550	958.881	86.381
1009.7	159.7	3563.855	3.7509	950.129	86.289
1009.7	159.5	3559.091	3.7419	951.122	86.488
1081.7	144.6	3578.233	3.8275	934.861	93.769
1139.7	151.6	4144.944	4.1463	999.665	95.639
1221.7	157.5	4489.967	4.5638	983.820	90.597
1221.7	156.7	4455.537	4.5505	979.126	90.625
1317.7	147.3	3653.621	4.8373	755.291	74.369
1413.7	140.0	2650.769	5.0314	526.837	54.579
1615.7	132.5	1401.536	5.2578	266.560	29.178
1818.7	125.3	815.006	5.3184	153.240	17.737
2021.7	112.2	468.467	5.1552	90.871	11.746
2024.7	111.0	458.927	5.1340	89.388	11.679
2024.7	110.0	454.335	5.1035	89.023	11.738

TABLE XXXVII

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
TEMPERATURE (K) = 333.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
415.5	205.6	429.245	1.5222	281.983	19.892
415.5	204.1	425.893	1.5191	280.352	19.922
415.5	201.4	417.151	1.5191	274.597	19.775
415.5	197.7	406.962	1.5004	271.229	19.898
517.5	188.2	449.715	1.7275	260.319	20.061
617.5	195.8	543.574	1.9835	274.039	20.299
810.5	200.5	623.311	2.1822	285.631	20.662
810.5	200.4	622.585	2.1800	285.578	20.668
1015.6	196.8	705.873	2.4982	282.543	20.822
1215.6	193.1	765.084	2.7631	276.890	20.797
1414.6	188.9	798.078	2.9775	268.035	20.579
1414.6	187.2	789.815	2.9768	265.315	20.555
1414.6	186.5	780.994	2.9666	263.255	20.472
1614.6	179.2	784.009	3.1571	248.328	20.098
1614.6	177.6	777.186	3.1658	245.491	20.048
1614.6	177.2	770.474	3.1484	244.717	20.030
1813.6	155.7	693.393	3.3456	207.252	19.306
1813.6	147.2	680.825	3.4837	195.427	19.255
1813.6	146.4	659.660	3.3714	195.660	19.384
1813.6	146.3	673.077	3.4674	194.115	19.244
1813.6	145.0	664.880	3.4542	192.481	19.253
1813.6	143.7	648.452	3.4144	189.913	19.168
2023.6	139.9	632.434	3.6306	174.194	18.059
2023.6	138.5	623.708	3.6086	172.835	18.099
2023.6	133.1	587.434	3.5323	166.299	18.121

TABLE XXXVII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
TEMPERATURE (K) = 303.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
415.4	190.1	480.721	1.4711	326.776	24.931
416.4	190.3	482.089	1.4711	327.706	24.976
614.4	191.0	663.794	1.9433	341.578	25.938
614.4	190.1	660.030	1.9457	339.222	25.881
813.4	183.2	786.361	2.3147	339.711	26.894
813.4	182.2	780.798	2.3127	337.600	26.874
1013.4	189.5	986.420	2.7327	360.960	27.626
1211.4	190.1	1131.069	3.0777	367.501	28.038
1211.4	189.6	1127.485	3.0747	366.692	28.050
1211.4	189.1	1127.482	3.0747	366.691	28.124
1413.4	180.5	1158.717	3.3275	348.224	27.981
1413.4	180.2	1152.062	3.3187	347.140	27.940
1557.4	167.2	1070.390	3.3899	315.758	27.390
1557.4	166.2	1063.394	3.3925	313.445	27.353
1710.4	161.8	1020.516	3.4877	292.597	26.228
1710.4	160.3	1010.123	3.4877	289.617	26.204
1710.4	158.5	997.124	3.4851	286.104	26.180
1867.4	146.8	868.417	3.4864	249.081	24.609
1867.4	145.5	858.415	3.4550	248.452	24.766
2027.4	143.7	787.175	3.5163	223.863	22.594
2027.4	141.0	769.763	3.4968	220.128	22.643
2027.4	140.8	769.763	3.5072	219.476	22.608
2027.4	139.5	757.690	3.4968	216.675	22.527
2027.4	136.7	738.706	3.4753	212.553	22.551

TABLE XXXVII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
TEMPERATURE (K) = 283.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
223.4	111.6	174.517	0.8110	215.176	27.964
223.4	111.0	173.952	0.8052	216.024	28.226
273.4	133.0	264.477	1.0117	261.401	28.506
321.4	150.7	359.380	1.2139	296.033	28.481
425.4	188.2	606.380	1.5922	380.843	29.350
466.4	200.6	693.282	1.7002	407.761	29.482
562.4	192.7	804.377	1.9747	407.338	30.658
562.4	192.1	798.748	1.9699	405.459	30.612
713.4	195.9	1021.434	2.3521	434.260	32.151
859.4	181.2	1101.316	2.6018	423.289	33.881
1012.5	173.3	1210.317	2.8683	421.961	35.314
1163.5	163.1	1263.216	3.0843	409.551	36.419
1260.5	153.5	1231.207	3.1722	388.119	36.672
1413.5	161.0	1413.769	3.5158	402.114	36.224
1558.5	146.7	1252.298	3.5848	349.327	34.537
1711.5	147.5	1228.014	3.7993	323.220	31.782
1865.5	137.4	1010.529	3.7993	265.977	28.076
1865.5	134.6	988.668	3.7993	260.223	28.040
2011.5	140.9	945.761	3.9640	238.586	24.559

TABLE XXXVII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
TEMPERATURE (K) = 263.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
225.3	109.4	214.927	0.8664	248.052	32.885
269.3	128.0	312.493	1.0551	296.156	33.557
321.3	149.7	453.404	1.2808	353.989	34.296
323.3	150.6	458.225	1.2881	355.729	34.259
416.3	189.8	796.971	1.7158	464.481	35.493
420.4	196.0	798.788	1.6800	475.448	35.182
561.4	195.4	1072.526	2.1017	510.301	37.877
615.4	179.2	1064.553	2.1778	488.818	39.563
760.4	183.2	1410.298	2.5827	546.039	43.229
912.4	169.5	1615.325	2.8861	559.678	47.890
1005.4	134.9	1379.476	2.9538	467.014	50.211
1161.4	144.8	1833.884	3.4423	532.736	53.361
1261.4	157.2	2202.372	3.8259	575.647	53.111
1261.4	155.2	2162.717	3.8081	567.911	53.072
1261.4	150.5	2058.315	3.7364	550.873	53.088
1408.4	146.1	1966.599	4.0306	487.915	48.436
1565.4	145.3	1700.205	4.2212	402.774	40.204
1565.4	144.8	1694.263	4.2180	401.668	40.232
1706.4	142.0	1395.804	4.3458	321.179	32.805
1706.4	140.0	1373.656	4.3458	316.083	32.745
1856.4	132.2	1018.697	4.3264	235.460	25.832
1856.4	131.4	1006.008	4.3310	232.279	25.638
2015.4	118.8	681.711	4.1915	162.639	19.855
2016.4	119.2	686.333	4.2433	161.743	19.680
2016.4	118.7	684.337	4.2106	162.524	19.858

TABLE XXXVII (continued)

TABULATED EXPERIMENTAL ISOTHERMAL DATA FOR
EQUIMOLAL MIXTURE OF CO2-CH4-N2-C2H6
TEMPERATURE (K) = 243.15

PI	ΔP	POWER	FLOW	ΔH	-(ΔH/ΔP)
PSIA	PSI	J/MIN	MOL/MIN	J/MOL	J/MOL-BAR
223.4	104.0	255.639	0.9013	283.622	39.553
269.4	122.0	377.421	1.1046	341.653	40.616
319.4	143.2	548.625	1.3351	410.917	41.619
365.4	161.0	751.365	1.5612	481.252	43.353
439.4	176.3	1037.230	1.8588	557.999	45.905
439.4	121.0	623.234	1.5938	391.021	46.870
1310.8	135.0	1159.172	3.2608	355.487	38.191
1310.8	133.3	1127.835	3.2622	345.727	37.617
1413.8	127.0	1000.310	3.2009	312.505	35.689
1413.8	124.2	976.829	3.1994	305.307	35.653
1563.8	131.7	756.385	3.3628	224.924	24.770
1714.8	127.0	522.315	3.4583	151.030	17.248
1863.8	145.0	483.065	3.7040	130.416	13.045
1863.8	143.0	480.100	3.7101	129.401	13.124
2015.8	133.0	321.090	3.5498	90.452	9.863
2015.8	131.8	317.981	3.5063	90.687	9.979

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